Pressure Induced Structural Transition in the Solid-Solution La$_{2-x}$Nd$_x$CuO$_4$ for x = 0.6, 0.7, 1.2, and 1.5

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A pressure induced transition from the T′ to the T/O structure has been observed in the La$_{2-x}$Nd$_x$CuO$_4$ solid-solution for x = 0.6, 0.7, 1.2, and 1.5 with energy dispersive X-ray diffraction. Indications have been found that such a transition may even occur in the x = 2.0 composition at pressure higher than 18 GPa. In all cases the observed transitions were reversible. The transition pressure has been related to the compressive stress in the Ln–O$_{II}$ linkages in the fluorite-like LnO$_2$ layers of the T′ structure. The pressure dependence of the tolerance factor t is deduced and discussed. A strong electrostatic repulsion between oxygen ions in the 4d site is probably responsible for the increase of the T′ structure's bulk modulus with Nd content x.   © 1996 Academic Press, Inc.

I. INTRODUCTION

Depending on the size of the lanthanide ion the Ln_2CuO$_4$ cuprates (Ln = rare earth) crystalline in either of two different structures. La$_2$CuO$_4$ is the only compound of this series able to adopt the tetragonal K$_2$NiF$_4$ (T) structure ($I4/mmm$) which either occurs above 573 K (at ambient pressure) or at a pressures above 3.4 GPa (at room temperature) (1, 2) (see Fig. 1). Under normal conditions (P = 1 bar and room temperature) the T structure is orthorhombically distorted due to a small tilt of the Cu–O octahedra, and hence forming the so called T/O structure ($Abma$). Substituting the other lanthanide from praseodymium to thulium instead, results in compounds which crystallize in the related T′ structure ($I4/mmm$) (3). In both the T and T′ structures the cations and one half of the oxygen ions (labeled O$_I$) occupy the same positions (see Fig. 1). However, the arrangement of the other half of the oxygen atoms (labeled O$_{II}$) is quite different in both structures, resulting in different coordination polyhedra. In the T/O structure the Ln^{3+} and Cu^{2+} ions have, respectively, a ninefold and sixfold (elongated octahedron) coordination, whereas they occupy an eightfold (pseudo-cubic) and fourfold (square-planar) coordinated site in the T′ structure. The consequence of the lower coordination number in the T′ structure is a larger volume per formula unit, despite the smaller size of the lanthanide ions. Both structures induce very interesting physical properties, mainly superconductivity when they are either p- (T/O) or n-doped (T′).

The stability of the different structures can be evaluated from the tolerance factor $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ defined by Goldschmidt in the related perovskite-type structure (4, 5), where r_A, r_B, and r_O are the ionic radii of the lanthanide, the copper, and the sixfold coordinated oxygen ions, respectively. For the La$_{2-x}$Nd$_x$CuO$_4$ solid-solution t can be expressed in terms of x by using an average lanthanide ionic radius. So far the following phase diagram under normal conditions has been obtained (6, 7): (i) the T structure exists for $0.88 \leq t \leq 0.99$, (ii) the T/O structure is present for $0.865 \leq t < 0.88$, (iii) the T′ structure is stable for $0.83 \leq t < 0.865$, and (iv) for $t < 0.83$ a mixture of Ln_2O$_3$ and a new compound with the formula Ln_2Cu$_2$O$_5$ is found (7, 8). Based on the latter structure, however, a special treatment of such a mixture at high pressure and high temperature has allowed the stabilization of the T′ structure down to $t = 0.814$ (for Ln = Tb, Dy, Ho, Er, Tm) (9).

Given the difference in the volume per formula unit between the T/O and T′ structures and the coordination number of the lanthanide, pressure is likely to transform the T′ structure into the more compact and higher coordinated T/O. For the composition La$_{1.4}$Nd$_{0.6}$CuO$_4$ this transition was indeed observed around 10 GPa (10). Under normal conditions this composition is close to the borderline of stability of the T′ structure (7, 11). With increasing Nd content x the tolerance factor t decreases and the T′ structure becomes more stable. This suggests that the T′ → T/O transition in Nd-rich compositions is most likely to occur at higher pressures. To examine the pressure induced structural transformation we performed energy dispersive X-ray diffraction (EDXRD) measurements on various compositions of the La$_{2-x}$Nd$_x$CuO$_4$ solid-

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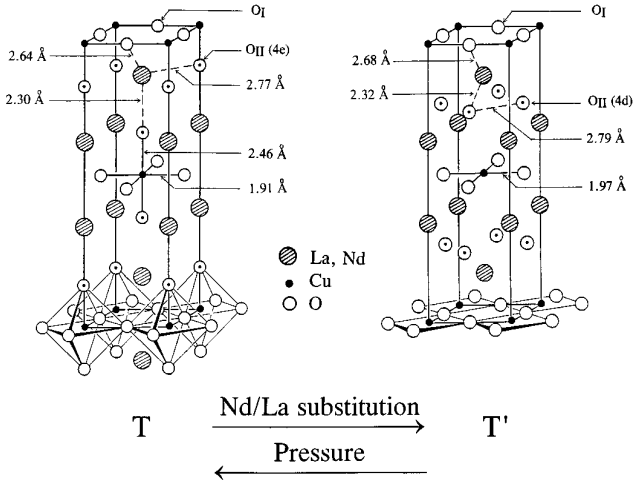
FIG. 1. Schematic view of the T (K₂NiF₄) and T' (Nd₂CuO₄) structure. The T/O structure of La₂CuO₄ is deduced from the T structure by an orthorhombic distortion of the unit cell due to a slight tilt of the Cu–O octahedra. In the $La_{2-x}Nd_xCuO_4$ solid-solution a structural transition from the T/O to the tetragonal T' structure is achieved by substituting Nd for La ($x > \approx 0.4$). Applying pressure to the T' structure can induce a transition to the T/O phase. The given interionic distances correspond to those in La₂CuO₄ and Nd₂CuO₄, respectively (1, 3, 7).

solution (x = 0.6, 0.7, 1.2, 1.5, and 2.0) under hydrostatic pressure.

II. EXPERIMENTAL

The polycrystalline samples of $La_{2-x}Nd_xCuO_4$ were synthesized from the coprecipitation in an alkaline medium of high purity chlorides of the respective cations, following the experimental procedure described in detail elsewhere (10, 12). The resulting products were identified by X-ray diffraction, using a conventional powder diffractometer (CuKα and $\theta < 50°$). The high pressure experiments were performed using a diamond anvil cell (DAC) and energy-dispersive X-ray diffraction (13). The diffraction patterns were recorded by means of a semiconductor detector. A well powdered specimen was filled into a 0.35 mm bore, which was drilled into a stainless steel gasket. The gasket was placed between the two diamonds of the DAC. The pressure was determined with the ruby luminescence technique (14) and the nonlinear ruby pressure scale (15). Silicone oil served as pressure transmitting medium. As a consequence the pressure conditions under which the experiments were carried out remained hydrostatic up to approximately 15 GPa. Under these circumstances the experimental error in determining the pressure is less than 0.2 GPa.

III. EXPERIMENTAL RESULTS

Figure 2 shows the EDXRD spectra of $La_{1.4}Nd_{0.6}CuO_4$ at ambient pressure and 15.2 GPa. In addition to the dif-

fraction peaks the K_α-fluorescence lines of La and Nd are distinctly present. For this composition the T' structure is stable up to 4.4 GPa. Above this critical pressure the crystal structure shows a clear phase transition to the T/O structure. The splitting of the (103) line into the (113) and (200) lines is a clear identification of this structural transformation. Additional proof can be found by comparing the change in position and shape of the diffraction peaks in the energy range between 22 and 32 keV. Describing the EDXRD spectra by a superposition of several pseudo-Voigt profiles the positions of the diffraction peaks were determined. The lattice parameters were calculated by a least square fit using the so obtained peak positions.

The corresponding volume–pressure data of $La_{1.4}Nd_{0.6}CuO_4$ are plotted in Fig. 3a. The phase transition at $P_T = 4.4$ GPa is accompanied by a volume decrease of about 3.5%. We used the inverted Murnaghan equation of state to describe the $V(P)$ dependence in the T' phase, and obtained a bulk modulus $B_0 = 152(12)$ GPa using the fixed
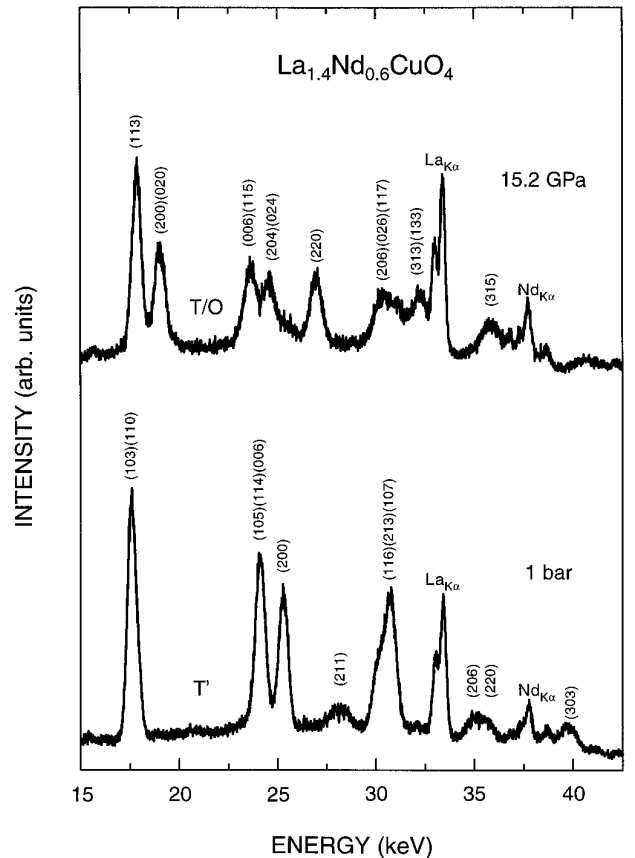
FIG. 2. EDXRD spectra of $La_{1.4}Nd_{0.6}CuO_4$ at ambient pressure and 15.2 GPa. The lines are indexed according to the T' (low pressure phase) and the T/O (high pressure phase) structure. In addition to the diffraction peaks K_α-fluorescence lines of La and Nd are present. The splitting of the (103) line into the (113) and (200) lines clearly indicates the structural transformation.
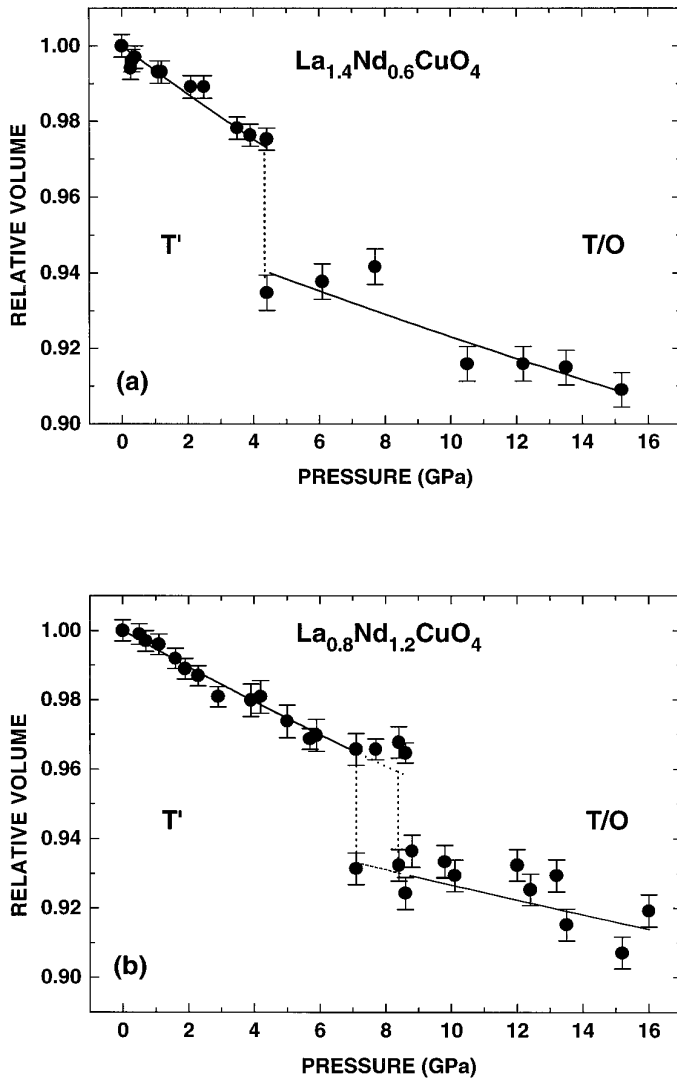
FIG. 3. (a) Relative unit-cell volume versus pressure for $La_{1.4}Nd_{0.6}$ CuO_4. The solid line represents an equation of state using $B_0 = 152(12)$ GPa and $B_0' = 4$. (b) $V(P)$ diagram for $La_{0.8}Nd_{1.2}CuO_4$. The solid line for the low pressure phase represents an equation of state using $B_0 = 185(16)$ GPa and $B_0' = 4$. In the pressure range between 7.0 and 8.4 GPa an indexing in both the T' and T/O structures was possible, i.e., both phases seem to coexist.

value $B_0' = 4$. This particular composition showed a very sharp phase transition; i.e., the structural transformation occurred within a pressure range of about 0.5 GPa. This, however, is not the case for the other compositions studied in this work. As an example, we present in Fig. 3b the $V(P)$ diagram of $La_{0.8}Nd_{1.2}CuO_4$. Around 7.0 GPa first signs of the transition have been found in the EDXRD spectra. These consist of a broadening of the (103) line and of additional features in the energy range between 22 and 32 keV, similar to those mentioned above. An indexation either in the tetragonal (T') or in the ortho-

rhombic structure (T/O) was possible yielding different lattice parameters and hence a different unit-cell volume. Above 8.4 GPa only an indexation in the T/O structure was possible. Based on this observation, we assume that the phase transition starts at about 7 GPa and is completed at 8.4 GPa. In this pressure range both phases seem to coexist. As the corresponding P_T value we used the average value of 7.7 GPa which is in the middle of the transition region, and as the error we have taken half the width (0.7 GPa) of this region. The volume decrease at the transition is found to be about 2.8%. Fitting the T' data to the inverted Murnaghan equation we obtained $B_0 = 185(16)$ GPa when B_0' was fixed to 4.

The $V(P)$ diagrams of $La_{1.3}Nd_{0.7}CuO_4$ and $La_{0.5}Nd_{1.5}$ CuO_4 show qualitatively the same behavior as those presented in Fig. 3b. In these compounds the phase transformations were accompanied by a volume decrease of 5.2 and 4.2%, respectively. For the ternary oxide Nd_2CuO_4 itself, however, no clear evidence for a phase transition has been found. Nevertheless, comparing the EDXRD spectra obtained at 17 and 22 GPa, first indications of the T' → T/O transition were present. Although the same features have been identified as a precursor of the T/O structure in the other compounds, no clear signs of the structural transformation have been observed in the spectrum of Nd_2CuO_4 up to 25 GPa, the limit of our DAC. It is very likely that evidence of a structural transformation may actually occur at higher pressures. For these compounds we also calculated the B_0 value (see Table 1), which is in particular very high for Nd_2CuO_4. This results from the fact that we have not that many data points in the T' phase of Nd_2CuO_4. Therefore, the equation of state did not fit to the data as well as for the other data sets, but the bulk moduli found for the $La_{2-x}Nd_xCuO_4$ compositions with $x \leq 1.2$ are comparable with other ternary oxides ((16, 17) and references therein).

In Fig. 4 the transition pressure P_T is plotted versus the tolerance factor t. We have chosen t as variable because it takes the Ln–O and Cu–O ionic bonding and coordination into account and gives an estimate of the structural stability. Nevertheless, the Nd content x can also be used. The t factor is obtained by using an average lanthanide ionic radius $r_A = 0.5[(2 - x)r_{La^{3+}} + xr_{Nd^{3+}}]$, with $r_{La^{3+}} = 1.216$ Å and $r_{Nd^{3+}} = 1.163$ Å (in this work Shannon's ionic radii (18) were used). According to the definitions of t and the average radius r_A, a linear relation between t and x exists. For the sake of consistency, the t values of the T' and T/O structures have been calculated using rare earth ions in a ninefold and copper and oxygen ions in a sixfold coordination. Fitting the data to a linear $P_T(t)$ dependence (solid line in Fig. 4) and extrapolating it down to $P_T = 0$ GPa yields $t = 0.8662$. This value is higher than $t = 0.865$ which represents the border of stability of the T' structure. Extrapolating the assumed linear behavior down to the t

TABLE 1

Tolerance Factor, Unit-Cell Volume, and Lattice Parameters at Ambient Pressure as Well as Bulk Modulus
and Phase Transition Pressure P_T for Several Compositions of the $La_{2-x}Nd_xCuO_4$ Solid-Solution

Composition	t^a	$V_0(\text{Å}^3)$	$a_0(\text{Å})$	$c_0(\text{Å})$	$B_0(\text{GPa})$	$P_T(\text{GPa})$
$La_{1.4}Nd_{0.6}CuO_4$	0.8632	98.5(4)	3.982(4)	12.422(1)	152(12)	4.4(5)
$La_{1.3}Nd_{0.7}CuO_4$	0.8623	98.2(3)	3.980(2)	12.400(6)	171(39)	6.2(6)
$La_{0.8}Nd_{1.2}CuO_4$	0.8579	96.7(4)	3.965(5)	12.302(2)	185(16)	7.7(7)
$La_{0.5}Nd_{1.5}CuO_4$	0.8553	95.8(4)	3.954(4)	12.259(1)	264(40)	13.6(25)
Nd_2CuO_4	0.8509	94.7(2)	3.944(2)	12.171(1)	357(56)	≥ 18

^{a} The tolerance factor t is calculated using ionic radii with Cu^{2+} and O^{2-} in sixfold and Ln^{3+} in ninefold coordination (18).

value of Nd_2CuO_4 ($t = 0.8509$) gives as a first estimate $P_T \approx 18$ GPa. This extrapolated pressure is close to the value were we have seen first indications for a T′ → T/O transition. Therefore, we have additional confidence that the observed features in the EDXRD spectra of Nd_2CuO_4 can be interpreted as a precursor of the phase transition.
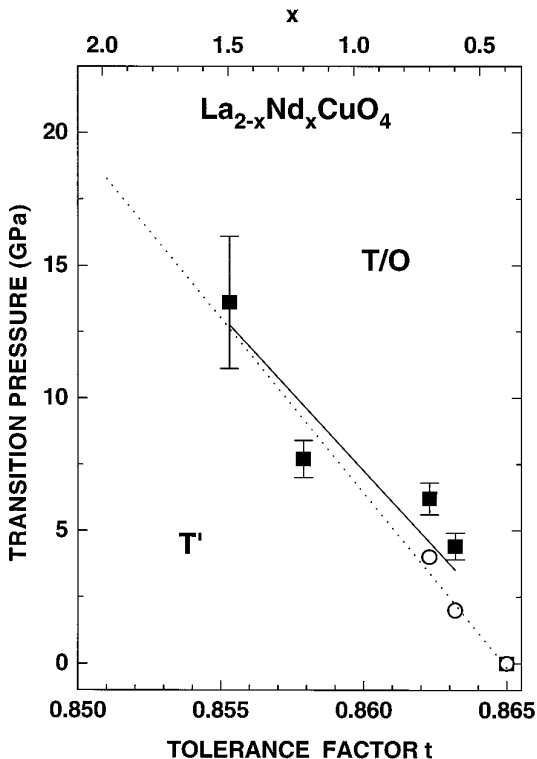

FIG. 4. Transition pressure P_T as a function of the tolerance factor t and the Nd content x. Squares represent measured data. The solid line is a linear fit to the measured data including the point at $t = 0.865$. An extrapolation to $P = 0$ GPa gives $t = 0.8662$ as the maximum t value for the T′ structure. The data points at $t = 0.8632$ and $t = 0.8623$ represent corrected data (see text). The dotted line yields $t = 0.8649$ at $P_T = 0$ which is in very good agreement with the t value at the limit of the T′ phase. An extrapolation to smaller t values gives an estimate for the minimum pressure needed to transform Nd_2CuO_4 into the T/O structure.

However, further experiments at pressures higher than 25 GPa are necessary to give a definite answer to whether such a phase transition indeed occurs in Nd_2CuO_4. The deviation of our extrapolated t value for $P_T = 0$ from that known suggests that the transition pressure for $La_{1.4}Nd_{0.6}CuO_4$ and $La_{1.3}Nd_{0.7}CuO_4$ may be overestimated and this may be closely related to the way we have estimated P_T.

Experiments during pressure release revealed the existence of a hysteresis loop in the $V(P)$ diagram. The orthorhombic phase persisted down to pressures far below P_T, but in each case the low pressure phase eventually was reached again at low enough pressures. The presence of this large hysteresis loop involves that the reported P_T values do not correspond to an equilibrium. In order to get a better estimate for an equilibrium pressure (middle of the hysteresis loop), carefully performed experiments on releasing pressure have to be done.

Using the $P_T(t)$ data the pressure dependence of the tolerance factor can be estimated (see Fig. 5). The boundaries for the different phases are known and given in Section I, and the t values at $P = 0$ GPa are listed in Table 1. For La_2CuO_4 we used $t = 0.8684$. Assuming that at the T′ → T/O transition the tolerance factor has to be $t = 0.865$ (19), we get a first estimate of the pressure dependence of t. As seen in Fig. 5 the $t(P)$ curves are divided in two parts. The smaller slopes for $La_{1.4}Nd_{0.6}CuO_4$ and $La_{1.3}Nd_{0.7}CuO_4$ appear anomalous. This can be interpreted as another sign that the P_T values may be overestimated.

IV. DISCUSSION

The influence of high pressure on the T′ structure can be understood qualitatively in considering the coordination number of the rare earth ions and the density of the structure. As pressure is applied the density increases and a higher coordination number is favored. Hence the T′ → T/O transition is very likely to occur. But to understand the observed increase of P_T as t decreases we have to look at the $La_{2-x}Nd_xCuO_4$ phase diagram and especially at the $Ln-O_{II}$ and $O_{II}-O_{II}$ interactions.
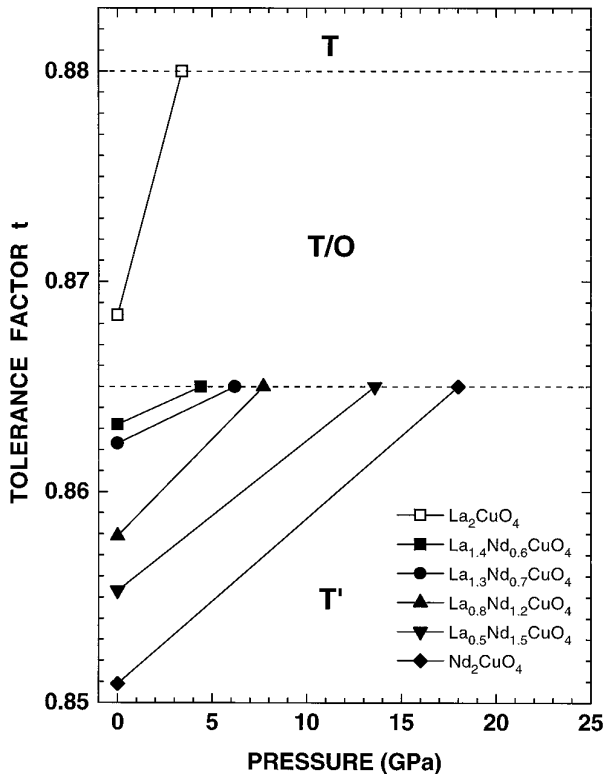
In the T/O structure compressive and tensile forces are

FIG. 5. Tolerance factor t versus pressure. The $t(P)$ curves seem to split into two parts. The small pressure dependence of t for $La_{1.4}Nd_{0.6}CuO_4$ and $La_{1.3}Nd_{0.7}CuO_4$ probably results from an overestimation of P_T (see text). The $t(P)$ curves may be used for an estimate of the pressure needed to induce the T/O → T transition in the $La_{2-x}Nd_xCuO_4$ solid-solution. The $t(P)$ value of La_2CuO_4 is taken from Ref. (2).

present in the basal CuO_2 plane and the $(LnO)_2$ rock salt-like layer, respectively. For La_2CuO_4 the interionic $Cu-O_I$ distances ($a/2 \approx 1.91$ Å) are shorter than the sum of the ionic radii (2.13 Å, with $r_{Cu^{2+}} = 0.73$ Å and $r_{O^{2-}} = 1.40$ Å) leading to a compression. The two $Cu-O_{II}$ distances are significantly longer (2.46 Å, using $c = 13.15$ Å (1, 7)). The tension is due to the fact that eight out of nine $Ln-O$ interionic distances are longer (≈ 2.64 Å for $Ln-O_I$ and ≈ 2.77 Å for $Ln-O_{II}$) and only the distance between the lanthanide and the apical oxygen (≈ 2.30 Å) is shorter than the sum of the ionic radii (2.62 Å, using $r_{La^{3+}} = 1.216$ Å). Both kinds of stresses are partially relieved by a cooperative tilting of the octahedra resulting in the orthorhombic distortion (i.e., the T → T/O transition).

While the average size of the lanthanide decreases by Nd substitution ($r_{Nd^{3+}} = 1.163$ Å) the tolerance factor t also decreases. When the critical value $t = 0.865$ is reached, the O_{II} ions move from the 4e sites of the T/O structure (0, 0, z; 0, 0, −z) to the 4d sites (0, 0.5, 0.25; 0.5, 0, 0.25) of the T′ structure (see Fig. 1). The T/O → T′ transition as a function of the average lanthanide ion size has been interpreted as optimization of the $Ln-O$ distances (5–7).

The average $Ln-O$ distance in the T′ structure is significantly shorter (2.51 Å instead of 2.64 Å) in the resulting fluorite-like arrangement compared to the rock salt-like layer in the T/O structure. Among the eight $Ln-O$ distances in the T′ structure, four are significantly shorter (2.32 Å, for $Ln-O_{II}$) and four are longer (2.68 Å, for $Ln-O_I$) than the sum of the ionic radii (2.51 Å). Therefore, a compression in the $Ln-O_{II}$ linkages is present. Furthermore, the oxygen ions at the 4d site are separated only by $a/\sqrt{2}$ (≤ 2.81), which is very close to the sum of the ionic radii (2.80 Å). To diminish the $O_{II}-O_{II}$ repulsion, the structure has to expand along the a and b axis. As a consequence the CuO_2 layers in the T′ structure are under tension. The expansion in the a, b plane is not compensated by a sufficient decrease in the c parameter which hence results in a considerably larger unit-cell volume as compared to the T/O structure. Considering the smaller average rare earth size this is not expected.

$La_{1.4}Nd_{0.6}CuO_4$ is very close to the borderline of stability of the T′ structure. A moderate pressure (4.4 GPa) is sufficient to induce the structural transformation. At ambient pressure the above reported compressive stress in the $Ln-O_{II}$ linkages is the strongest in $La_{1.4}Nd_{0.6}CuO_4$ due to the large average size of the lanthanide ions. This steric effect tends, on the other hand, to release the $O_{II}-O_{II}$ repulsive interaction. The compression of the structure under the effect of pressure increases the compressive stress in $Ln-O_{II}$ and results in a destabilization of the T′ structure in favor of the T/O one at rather low pressures. Further substitution of neodymium for lanthanum decreases the compressive stresses in $Ln-O_{II}$ and increases the $O_{II}-O_{II}$ repulsive interaction at ambient pressure. To achieve the compression of the $Ln-O_{II}$ linkage needed to induce the T′ → T/O transformation, a higher pressure has to be applied. For Nd_2CuO_4, in which the compressive stress in the $Ln-O_{II}$ linkages is the weakest and the $O_{II}-O_{II}$ interaction is the strongest, the highest pressure should be needed to achieve the transformation. Indeed, for Nd_2CuO_4 we found no clear transition up to 25 GPa, whereas all the other compounds studied have shown a phase transformation. Therefore the transition pressure can be related to the compressive stress in the $Ln-O_{II}$ linkages of the T′ structure at ambient pressure. Furthermore, this behavior is consistent with the observation, that the T/O → T′ structure, resulting from the substitution of Nd for La at ambient pressure, occurs to optimize $Ln-O$ distance (5–7). The effect of pressure on the T′ structure of a given composition is similar to that of the substitution of La for Nd (decreasing x) at ambient pressure in the same starting composition.

The structural changes can also be described in terms of a pressure dependent tolerance factor. In the $La_{2-x}Nd_x$ CuO_4 system we have found an increase in t with pressure (see Fig. 5). Such an increase is a consequence of the fact

that in this structure type the average Ln–O$_{II}$ bond is less compressible than the average Cu–O bond. As mentioned in Section III, the $t(P)$ curves are split in two parts. Considering the definition of P_T, the observed hysteresis, and the $P_T(t)$ fit (Fig. 4) the transition pressures for La$_{1.4}$Nd$_{0.6}$CuO$_4$ and La$_{1.3}$Nd$_{0.7}$CuO$_4$ may be overestimated. The other $t(P)$ dependencies are almost the same if we take the error bar for P_T in consideration. Taking an average of the latter $\partial t/\partial P$ values and using it for La$_{1.4}$Nd$_{0.6}$CuO$_4$ and La$_{1.3}$Nd$_{0.7}$CuO$_4$, the transition pressure shifts down to ≈ 2 GPa and ≈ 3 GPa, respectively. These values are plotted in Fig. 4 (circles) and used to fit a linear $P_T(t)$ dependence (dotted line). The t axis is now intersected at $P_T = 0$ GPa for $t = 0.8649$ which is in very good agreement to $t = 0.865$. Extrapolating this linear dependence toward smaller t values we get a transition pressure for Nd$_2$CuO$_4$ of $P_T \approx 18.5$ GPa.

Figure 5 can also be used to make estimates about a pressure induced T/O → T transition in the compounds studied in the present work. Such a transition which has been already found in La$_2$CuO$_4$ at 3.4 GPa (2) can be expected to occur in the La$_{2-x}$Nd$_x$CuO$_4$ compounds at higher pressures. However, by means of powder X-ray diffraction it will be difficult to resolve this transition, since the degree of the octahedral tilting is small in the T/O structure. Nevertheless, it would be very interesting to investigate the $t(P)$ diagram in more detail.

The simple picture described above can also be used to explain the increase of the bulk modulus B_0 for increasing x (see Table 1). Close to the stability line of the T′ structure (at $t = 0.865$), the separation of the O$_{II}$–O$_{II}$ ions is larger than the corresponding interionic distance. The compressibility of the a axis parameter ($\kappa_a \approx 1 \times 10^{-3}$ GPa^{-1}) is found to be three times smaller than that of the c axis. This anisotropy is well known for this class of materials (16, 17) and is attributed to the electrostatic repulsion between the oxygen ions at the $4d$ sites. The larger the Nd content, the closer are the O$_{II}$–O$_{II}$ distances to their corresponding sum of the ionic radii, already at ambient pressure. The unit cell is most compressible along the c direction and κ_a is smaller than for the Nd-poor compositions. As a consequence the bulk modulus is increasing with Nd content.

The reversibility of the transition shows that the T/O structure is not induced by a change in composition, but results only from the pressure effect. This can be concluded from the T′ → T/O transition in the La$_{2-x}$Nd$_x$CuO$_4$ solid-solution, which has been obtained in the composition range $0.60 \leq x \leq 0.75$ after treatment under oxygen pressure (40 MPa and 1183–1213 K) or electrochemical oxidation (12). In that case, the T/O structure is stabilized by the presence of extra oxygen species in the oxygen sublattice and therefore involves a change in composition and charge redistribution: La$_{2-x}$Nd$_x$Cu(II)$_{1-2\delta}$Cu(III)$_{2\delta}$O$_{4+\delta}$.

V. CONCLUSION

The pressure induced, reversible T′ → T/O phase transition has been observed in La$_{2-x}$Nd$_x$CuO$_4$ solid-solution for $x = 0.6$, 0.7, 1.2, and 1.5. For Nd$_2$CuO$_4$ itself the phase transition has not been seen clearly but strong evidence has been found that it may occur at pressures higher than 18 GPa. The transition pressure increases as a function of the Nd content x and decreases with the tolerance factor t. This behavior is related to compressive stress in the Ln–O$_{II}$ linkages in the fluorite-type LnO$_2$ layers. The compressive stress decreases when the average lanthanide ion size is reduced. The structural changes can also be described in terms of a pressure dependent tolerance factor. The low compressibility of the basal plane results from the strong electrostatic repulsion between the O$_{II}$–O$_{II}$ ions which increases for increasing Nd content and causes the increase in the bulk modulus as well. These experiments show that a pressure-induced transition is likely to occur in other similar systems, provided that the average ionic size of the lanthanide is suitable.

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19. In this context the absolute value of t is not that important. The phase diagram is not perfectly clear yet. It seems that a narrow two phase region exists between the T/O and T′ phases (see, e.g., Fig. 2 in (7) and Fig. 1 in (11)). In this case the tolerance factor is slightly decreased.