

# Influence of pressure on the crystal structure of $\text{Nd}_2\text{CuO}_4$

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The pressure evolution of the crystal structure of  $\text{Nd}_2\text{CuO}_4$  (tetragonal  $T'$ -type) was studied at room temperature up to 36 GPa using synchrotron radiation. At  $P_T=21.5$  GPa a structural transformation into the T-structure (tetragonal  $\text{K}_2\text{NiF}_4$ -type) occurred. Upon releasing pressure a gradual distortion of the T-structure into the orthorhombic O-phase ( $Cmca$ ) was found in the pressure range  $10 < P < 18$  GPa, and at lower pressure the starting  $T'$ -phase was restored. The pressure evolution of the unit-cell parameters and the interatomic distances were determined by Rietveld refinement of the diffraction pattern.

## 1 Introduction

In a recent study<sup>1</sup> the structural evolution of the solid-solution  $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$  ( $T'$ -structure,  $I4/mmm$ ) under pressure was investigated for  $0.6 \leq x \leq 1.5$ . At a pressure  $P_T$  new lines in the energy-dispersive diffraction pattern appeared, indicating a structural phase transition. The transition pressure  $P_T$  increases with the Nd content  $x$ . The  $P_T(x)$  dependence was related to compressive stress in the Ln–O<sub>2</sub> linkages of the fluorite-type LnO<sub>2</sub>-layers in the  $T'$ -structure. The compressive stress decreases when the average lanthanide ion size is reduced, *i.e.*  $x \rightarrow 2$ . The pressure effects were also described in terms of a pressure dependent tolerance factor  $t$ , defined by Goldschmidt<sup>2</sup> to describe the stability of the related perovskite structure. For the solid solution  $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$  it was found that the transition pressure  $P_T$  increases as  $t$  decreases.<sup>1</sup>

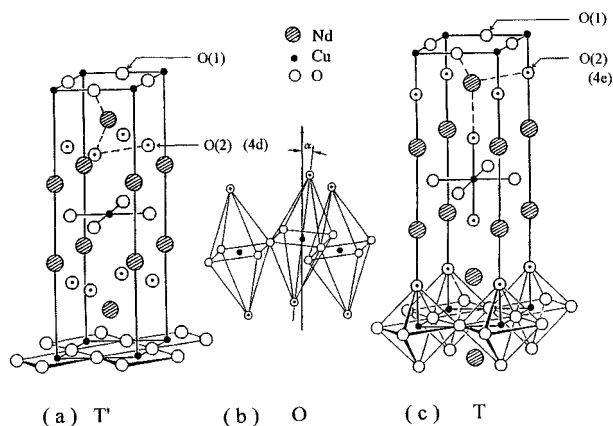
In the  $T'$ -structure of  $\text{Nd}_2\text{CuO}_4$  the Cu-ions at the origin (2a-site) are surrounded by four oxygen ions, labeled O(1) in Fig. 1(a), which occupy the 4c-site.<sup>3</sup> The lanthanides at the 4e-site have eight nearest oxygen-ion neighbours [O(2) at 4d-site] in a pseudo-cubic symmetry. As pressure is applied to this structure, the O(2) ions are forced to the 4e-position whereas the other ions remain at their sites. In the high

pressure O-phase [distorted  $\text{K}_2\text{NiF}_4$ -type, Fig. 1(b)] or T-phase [ $\text{K}_2\text{NiF}_4$ -type, Fig. 1(c)] the Ln<sup>3+</sup> and the Cu<sup>2+</sup> ions have now a nine- and a six-fold (elongated octahedron) oxygen coordination, respectively. Owing to the poor resolution of the observed lines in the energy-dispersive X-ray study of  $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ <sup>1</sup> it was not possible to determine whether the high pressure phase was distorted or not. It was assumed that the same phase sequence ( $T' \rightarrow O \rightarrow T$ ) is followed as was found for the tolerance factor.<sup>4,5</sup> In the O-phase the CuO<sub>6</sub> octahedra rotate cooperatively about the [110] axis and the crystal structure is orthorhombic. This structure is found for  $\text{La}_2\text{CuO}_4$  at low pressure ( $P < 3.4$  GPa) and ambient temperature<sup>6</sup> or at low pressure ( $T < 573$  K) and ambient pressure.<sup>7</sup>

For  $\text{Nd}_2\text{CuO}_4$  itself first indications of a pressure induced structural change were found around 20 GPa<sup>1</sup> which was at the limit of the pressure device used. The experiments presented here were performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble. The accessible pressure range was much higher and the high flux of the synchrotron radiation should give diffraction patterns which reveal a better insight into the structural changes and should allow one to determine the symmetry of the high pressure phase.

## 2 Experimental

The polycrystalline sample of  $\text{Nd}_2\text{CuO}_4$  was synthesised by high temperature reaction of stoichiometric amounts of the oxides CuO and Nd<sub>2</sub>O<sub>3</sub> in air at 950 °C during 24 h, followed by a second treatment at the same conditions after intermediate grinding. The resulting product was identified by X-ray diffraction, using a conventional powder diffractometer (Cu-K $\alpha$  and  $\theta < 70^\circ$ ). The high pressure experiments were performed at ambient temperature using a membrane-type diamond anvil cell (DAC). A well powdered specimen was filled into a 0.125 mm bore, which was drilled in a stainless steel gasket. The gasket was placed between the two diamonds of the DAC. Nitrogen served as pressure transmitting medium. This ensured quasi-hydrostatic pressure conditions up to the highest pressure. The pressure was determined with the ruby luminescence technique<sup>8</sup> using the non-linear ruby pressure scale.<sup>9,10</sup> Under these circumstances the experimental error in determining the pressure was  $< 0.2$  GPa. The X-ray powder diffraction spectra were recorded using synchrotron radiation at the beamline ID09 at the ESRF. The high X-ray flux of the synchrotron combined with the image plate (size A3) provides

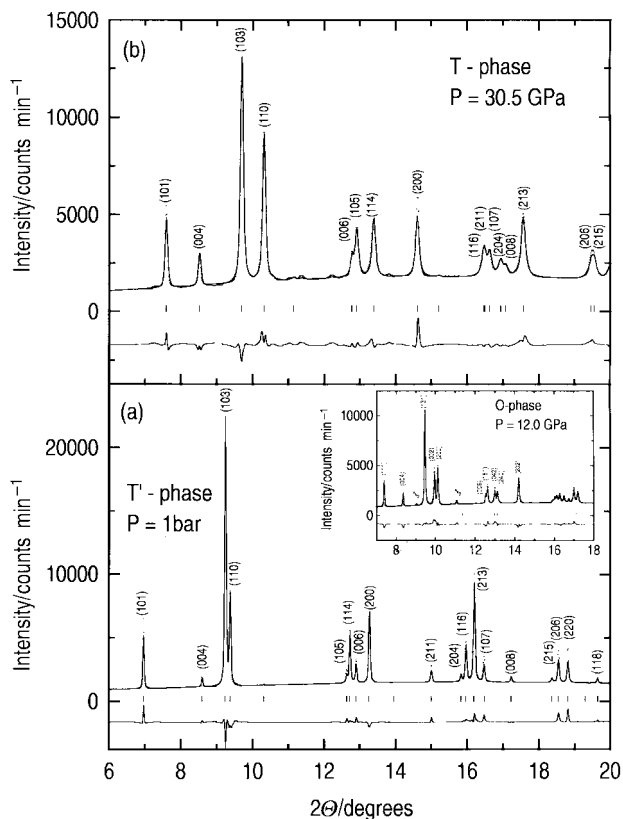


**Fig. 1** Schematic view of the structure of (a) the  $T'$ -phase (tetragonal,  $\text{Nd}_2\text{CuO}_4$ -type), (b) the O-phase (orthorhombic, distorted  $\text{K}_2\text{NiF}_4$ -type) and (c) the T-phase (tetragonal,  $\text{K}_2\text{NiF}_4$ -type) of the  $\text{Ln}_2\text{CuO}_4$  oxides (Ln=lanthanide). The oxygen atoms O(2) are distinguished from the O(1) ones by a central point.

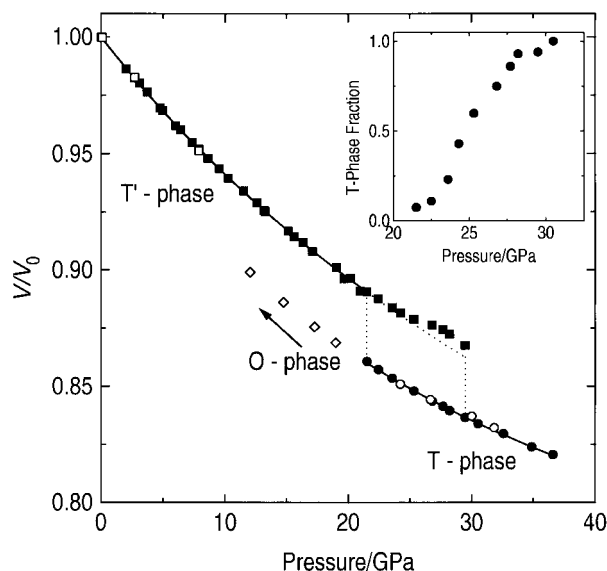
a much better resolution than the technique used in the recent investigation.<sup>1</sup> The diffraction images were collected at a wavelength of  $\lambda = 0.4558 \text{ \AA}$  ( $E \approx 25 \text{ keV}$ ) during 60 s exposure time. The images were integrated with the program *fit2d*.<sup>11</sup> The structural parameters and interatomic distances were obtained by Rietveld refinement<sup>12</sup> of the diffraction pattern in the range ( $3^\circ < 2\theta < 23^\circ$ ). Isotropic temperature factors were used for all atoms. In each pattern the temperature factors of the Nd and Cu atoms and those of the oxygen atoms were kept the same and these two parameters were refined independently. The  $N_2$  diffraction lines, originating from the pressure transmitting medium, were also refined.

### 3 Results and discussion

Fig. 2 shows diffraction patterns of  $Nd_2CuO_4$  at ambient pressure and  $P = 30.5 \text{ GPa}$ . At pressures up to  $P = 20 \text{ GPa}$  the tetragonal  $T'$ -phase is stable. In the pressure range  $21.5 < P < 31 \text{ GPa}$  a structural phase transformation into the tetragonal T-phase takes place gradually, which is clearly seen from the relative positions of some lines in the pattern recorded at  $30.5 \text{ GPa}$  in comparison to those in the pattern at ambient pressure [for example, (103) and (110), (114) and (200), (213) and (107)] [see Fig. 2(b)]. The pressure where first signs of the high pressure phase were observed is chosen as transition pressure, and therefore  $P_T = 21.5 \text{ GPa}$ . Upon releasing pressure, the T-phase exists down to  $\approx 18 \text{ GPa}$ . The gradual splitting of some characteristic lines [(110), (114), (213), ...] in the pressure range  $18 > P > 10 \text{ GPa}$ , indicates a distortion of the tetragonal T-phase into the orthorhombic (O) one. This is shown explicitly in the inset of Fig. 2 with a pattern obtained at  $12.0 \text{ GPa}$  and indexed according to the space group  $Cmca$ . Below  $8 \text{ GPa}$  the low pressure  $T'$ -phase was recovered again.



**Fig. 2** Powder diffraction pattern, refined and difference pattern as well as the peak positions of (a) the low pressure  $T'$ -phase ( $P = 1 \text{ bar}$ ) and (b) the high pressure T-phase ( $P = 30.5 \text{ GPa}$ ) of  $Nd_2CuO_4$ . In the inset the diffraction pattern of the orthorhombic O-phase, clearly indicated by the splitting of several lines, obtained on pressure release, is shown.



**Fig. 3** Relative unit-cell volume  $V/V_0$  of  $Nd_2CuO_4$  versus pressure. At  $P_T = 21.5 \text{ GPa}$  the  $T'$ -phase (bold squares) starts to transform into the high pressure T-structure (bold circles). The T-phase fraction increases with pressure as is depicted in the inset. Upon releasing pressure (open symbols) the orthorhombic O-phase (diamonds) appears and at low pressure the  $T'$ -phase (squares) is restored again.

The refinement of the diffraction pattern gave  $R_{wp}$  values between 3 and 6% and  $\chi^2 < 5$  (Table 1).

The  $V(P)$  diagram of  $Nd_2CuO_4$  is shown in Fig. 3. For the  $T'$ -phase the Murnaghan equation of state (EOS)<sup>13</sup>

$$V(P) = V_0 \left( \frac{B_0'}{B_0} P + 1 \right)^{-1/B_0'} \quad (1)$$

was adjusted to the data and a bulk modulus  $B_0 = 145(1) \text{ GPa}$  and its pressure derivative  $B_0' = 4.1(1)$ , with  $V_0 = 189.252(1) \text{ \AA}^3$  (solid line) and for the high pressure T-phase  $B_0 = 69(1) \text{ GPa}$  and  $B_0' = 8.7(1)$  were obtained, respectively. Using the Birch EOS<sup>14</sup>

$$P(V) = \frac{3}{2} B_0 \{ x^{7/3} - x^{5/3} \} \left[ 1 - \frac{3}{4} (4 - B_0') (x^{2/3} - 1) \right] \quad (2)$$

with  $x = V_0/V(P)$ , gives  $B_0 = 146(1) \text{ GPa}$  and  $B_0' = 4.0(2)$  for the  $T'$ -phase. Rather different values were obtained for the T-phase [ $B_0 = 56(5) \text{ GPa}$  and  $B_0' = 14(2)$ ].

The deviation of the extrapolated EOS (dotted line in Fig. 3) from the data points above  $P_T$  is interpreted as a sign of structural changes starting in this pressure range. Up to  $\approx 30 \text{ GPa}$  both the  $T'$ - and T-phase were used to refine the diffraction pattern. As shown in the inset of Fig. 3, the fraction of the T-phase, *i.e.* the high pressure form, increases in the transition region. It was also possible to use the orthorhombic structure to refine the pattern in this transition region. However, neither the  $R$ -values were improved nor the splitting of *e.g.* the (110) line was obvious. Therefore, the higher symmetry phase is used to describe the diffraction pattern. Above  $30 \text{ GPa}$  the pattern are well described using the T-phase only. The pattern recorded during pressure release showed a gradual and clear splitting [see inset of Fig. 2(a)] and the orthorhombic O-structure was used to refine the pattern. The corresponding  $V(P)$ -data are included in Fig. 3 (open diamonds). Below  $10 \text{ GPa}$  the same structural parameters were obtained as upon increasing pressure, indicating the reversibility of the structural changes. For each phase the lattice parameters, the unit-cell volume, the fractional coordinates, and the temperature factors are given in Table 1. The entries are chosen for the lowest (highest) pressure at which the T-structure (O-structure) were observed.

**Table 1** Symmetry, structural parameters, site symmetry, fractional coordinates, temperature factors (multiplied by 100),  $R_{wp}$  and  $\chi^2$  values of the ambient (T') and high pressure phases (T and O) of  $Nd_2CuO_4$ . The orthorhombic O-phase was obtained upon releasing pressure

T' ( <i>I4/mmm</i> ) $Z=2$ $P=1$ bar					T ( <i>I4/mmm</i> ) $Z=2$ $P=21.5$ GPa					O ( <i>Cmca</i> ) $Z=4$ $P=17.3$ GPa					
$a/\text{\AA}$	3.943(1)				3.629(3)				5.1374(4)						
$b/\text{\AA}$	3.943(1)				3.629(3)				12.450(1)						
$c/\text{\AA}$	12.1704(5)				12.40(2)				5.1815(4)						
$V/\text{\AA}^3$	189.252(1)				163.3(3)				331.32(3)						
atom	$x/a$	$y/b$	$z/c$	$U/\text{\AA}^2$	$x/a$	$y/b$	$z/c$	$U/\text{\AA}^2$	$x/a$	$y/b$	$z/c$	$U/\text{\AA}^2$			
Nd	4e	0	0	0.352(1)	0.9(1)	4e	0	0	0.387(3)	1.6(1)	8f	0	0.13(1)	0.49(1)	1.6(1)
Cu	2a	0	0	0.9(1)	0.9(1)	2a	0	0	0	1.6(1)	4a	0	0.5	0.5	1.6(1)
O(1)	4c	0	0.5	0	1.5(4)	4c	0	0.5	0	2.6(1)	8f	0	0.43(1)	0.51(2)	0.3(2)
O(2)	4d	0	0.5	0.25	1.5(4)	4e	0	0	0.16(2)	1.5(4)	8e	0.25	0.48(1)	0.25	0.3(2)
$R_{wp}$ (%)	4.8				5.4				5.7						
$\chi^2$	3.6				4.4				4.4						

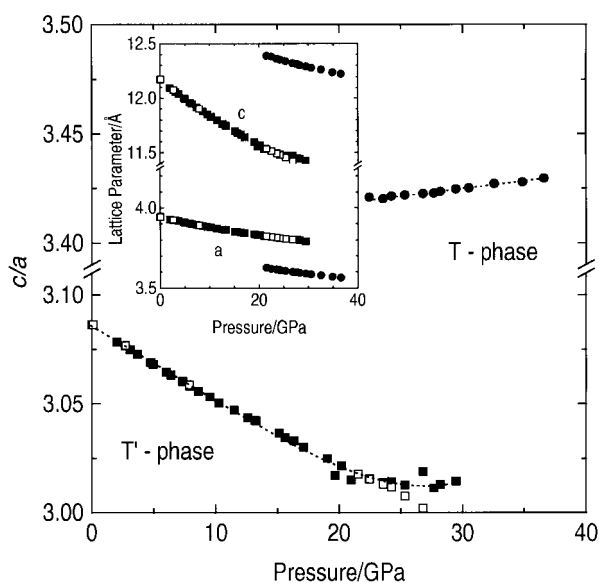
The transition pressure  $P_T=21.5$  GPa found for  $Nd_2CuO_4$  is in good agreement with the pressure where in a recent work<sup>1</sup> first signs of a structural transition were observed. Furthermore, this value gives additional support for the relation between  $P_T$  and the tolerance factor  $t$  to describe the stability of the  $La_{2-x}Nd_xCuO_4$  solid solution.<sup>1</sup> For  $Nd_2CuO_4$  the tolerance factor is  $t=0.8509$  and a transition pressure of about 20 GPa can be deduced from the  $P_T-t$  relation given in Fig. 4 of ref. 1. As the tolerance factor increases ( $t \rightarrow 1$ ) the phase sequence  $T' \rightarrow O \rightarrow T$  was obtained at normal conditions,<sup>4,5</sup> suggesting that under pressure the O-structure should occur before the T-phase. However, the refinement of the synchrotron data gave no evidence that the intermediate O-structure is attained upon increasing pressure. The T'-structure transforms in a relatively wide pressure range into the T-structure. During pressure release however, the O-structure is found at intermediate pressures before the T'-phase is finally formed at low pressure.

The T'-structure is more compressible along the  $c$ -axis than along the  $a$ -axis. This is seen from the  $c/a$ -ratio (Fig. 4) which decreases from 3.09 to  $\approx 3.01$  at the transition pressure. The pressure dependence of the lattice parameters (inset in Fig. 4) is described by the Murnaghan EOS and gives for the  $a$ - and  $c$ -axis  $B_0=527(3)$  GPa and  $B_0=326(4)$  GPa with  $B_0'=16.7(4)$

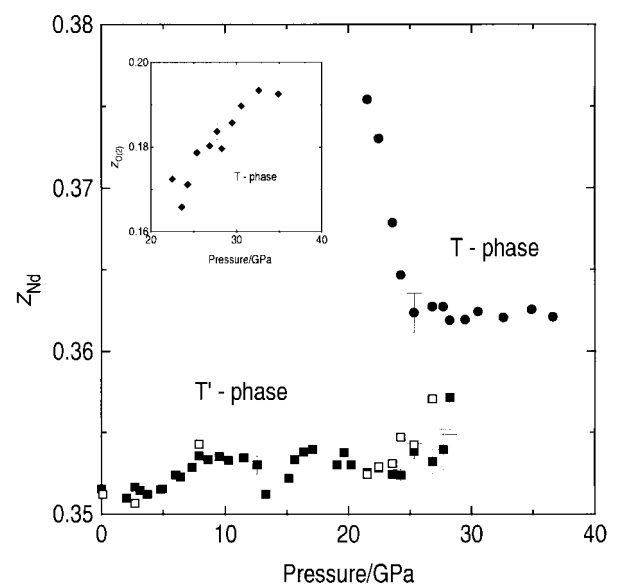
and  $B_0'=7.0(5)$ , respectively. The relative lattice parameter change at the transition is  $\approx -3\%$  and  $\approx +7\%$  for the  $a$ - and  $c$ -axis, respectively.

In the crystal structure of the T'-phase the only free parameter is the  $z$ -value of the Nd ion ( $z_{Nd}$ ). It is almost pressure independent up to  $P_T$  and jumps from  $z=0.352$  to  $z_{Nd}=0.387$  (Fig. 5). It strongly decreases down to  $z_{Nd}=0.362$  at  $P=27$  GPa and is then almost pressure independent up to the highest pressures. For the T-phase also the position of the oxygen ion O(2) is a free parameter ( $z_{O(2)}$ ). Its value increases monotonically with pressure from  $z_{O(2)} \approx 0.155$  at  $P_T=21.5$  GPa to  $\approx 0.195$  at  $P=36.6$  GPa (see inset Fig. 5).

For the pressure evolution of the crystal structure of  $Nd_2CuO_4$  a few interatomic distances are important. In the T'-phase the Cu-O(1) distance, *i.e.*  $d_{Cu-O(1)}=a/2=1.9717(5)$  Å at ambient pressure decreases to  $d_{Cu-O(1)}=1.9146(6)$  Å at 20.2 GPa. Its pressure dependence is given by that of the  $a$ -axis. The pressure dependence of the Nd-O(2) distance as well as that of Nd-O(1) are well described by the  $c$ -axis compressibility. As far as interatomic distances in the high pressure phase are concerned, the Nd-O(2) and Cu-O(2) distances are of particular interest because they determine the height of the  $CuO_6$ -octahedron. As is shown in Fig. 5, the



**Fig. 4** The  $c/a$ -ratio of  $Nd_2CuO_4$  versus pressure up to 36 GPa. In the inset the pressure variation of the  $a$  and  $c$  lattice parameter is shown for the T'- and T-phase. Open symbols represent data obtained during pressure release.



**Fig. 5** The fractional coordinate  $z_{Nd}$  in  $Nd_2CuO_4$  as function of pressure. Above 25 GPa the Nd-position in the T-phase is pressure independent. The inset shows the fractional coordinate  $z_{O(2)}$ . It increases with pressure, *i.e.* the  $CuO(2)$ -octahedron is enlarged along the  $c$ -axis.

fractional  $z$ -coordinate of Nd is rather pressure independent above 30 GPa and therefore the Nd–O(2) distance is determined through the pressure variation of  $z_{O(2)}$ . Above 30 GPa the Nd–O(2) distance decreases rather strongly ( $\approx -7\%$ ) and as a consequence the Cu–O(2) distance increases by the same amount. This means that the CuO<sub>6</sub> octahedron is elongated with increasing pressure.

#### 4 Conclusion

A structural phase transition from the low pressure T' to the high pressure T-phase was observed for Nd<sub>2</sub>CuO<sub>4</sub> at  $P_T = 21.5$  GPa at room temperature using synchrotron radiation. Above  $P_T$  the T-phase fraction increases and the transition is completed at 30 GPa. The transition pressure is in good agreement with the value predicted from the relation between  $P_T$  and the tolerance factor  $t$  of this system. An orthorhombic distorted O-phase was observed during pressure release in the range  $10 < P < 18$  GPa. This phase is not observed in the pattern upon increasing pressure due to hysteresis in the transition. At low pressure the initial T'-phase was found again.

#### 5 Acknowledgements

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