X-RAY INVESTIGATIONS OF \( \text{La}_2\text{CuO}_4 \) AND \( \text{Pr}_2\text{CuO}_4 \) UNDER HIGH PRESSURE

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Received 24 February 1989; revised manuscript received 2 October 1989; accepted for publication 10 October 1989
Communicated by D. Bloch

X-ray investigations of \( \text{Pr}_2\text{CuO}_4 \) and \( \text{La}_2\text{CuO}_4 \) under pressure have been carried out at 300 K and 30 K. The lattice parameters decrease monotonically for both structures, thus preserving the structure of the materials. For \( \text{La}_2\text{CuO}_4 \) the lattice parameter reduction is isotropic with increasing pressure, but the lattice parameters of \( \text{Pr}_2\text{CuO}_4 \) are found to behave anisotropically, as the \( c \)-axis decreases faster than the \( a \)-axis. \( \text{La}_2\text{CuO}_4 \) has a bulk modulus of 1850 kbar at 300 K, whereas \( \text{Pr}_2\text{CuO}_4 \) has a bulk modulus of 1600 kbar at 300 K and 1650 kbar at 30 K, due to the faster decreasing \( c \)-axis lattice parameter. In the \( a \) and \( b \) direction both materials have a similar compressibility. Assigning this behaviour to the common copper-oxide layers of both structures gives the possibility to generalize these results. For several high temperature superconductors we estimated the linear compressibilities in the \( a, b \) direction being in the range of 1.5 to \( 2.0 \times 10^{-4} \text{kbar}^{-1} \). In the \( c \)-direction the compressibility apparently depends on the degeneracy of the oxygen octahedra and the number of intercalated layers or structural elements.

1. Introduction

\( \text{La}_2\text{CuO}_4 \) has the \( \text{K}_2\text{NiF}_4 \) structure. At temperatures above 420 K it is tetragonal, but at lower temperatures it becomes orthorhombic [1]. There are small distortions of the \( a \)- and \( b \)-lattice parameters and the Cu–O octahedra are smoothly tilted. The structure is sketched in fig. 1a. For simplicity, we show the tetragonal unit cell, since the orthorhombic distortions are too small to be visible. If \( \text{La}_2\text{CuO}_4 \) is doped with Ba or Sr it is found to be superconducting [2], which was the starting point of the new high-\( T_c \) superconducting materials. With increasing content \( x \) of the dopant \( A=\text{Sr}, \text{Ba} \), \( \text{La}_{2-x}\text{A}_x\text{CuO}_4 \) becomes tetragonal [3,4] also at low temperatures. The superconductivity of \( \text{La}_2\text{CuO}_4 \) may also be induced by doping with excess oxygen, which ends in the formula \( \text{La}_2\text{CuO}_4+x \) [5,6]. For a more meaningful comparison of \( \text{La}_2\text{CuO}_4 \) with the non-superconducting \( \text{Pr}_2\text{CuO}_4 \) we decided to investigate the undoped and thus non-superconducting \( \text{La}_2\text{CuO}_4 \) rather than the doped \( \text{La}_2\text{CuO}_4 \).

\( \text{Pr}_2\text{CuO}_4 \) has a \( \text{Nd}_2\text{CuO}_4 \) structure [7], which is closely related to the \( \text{K}_2\text{NiF}_4 \) structure. The structure of \( \text{Pr}_2\text{CuO}_4 \) is shown in fig. 1b. The materials crystallizing in the \( \text{Nd}_2\text{CuO}_4 \) structure are tetragonal. The striking difference between the structures of \( \text{La}_2\text{CuO}_4 \) and \( \text{Pr}_2\text{CuO}_4 \) is the location of the oxygen \( \text{O}(\text{II}) \) site [8]. These oxygen atoms are marked in fig. 1. In \( \text{La}_2\text{CuO}_4 \) these oxygen atoms complete the octahedral coordination of the copper atom, whereas due to the change of the location of the oxygen atoms at the \( \text{O}(\text{II}) \) site, the Cu-atoms have a square planar environment in \( \text{Pr}_2\text{CuO}_4 \).

The structural investigation of these two materials may give a clue to the observed anisotropic pressure...
X-ray investigations of the sample in the pressure range up to 300 kbar [15]. The pressure determination was carried out by using the standard ruby fluorescence method [16]. The temperature was varied from 30 to 300 K for Pr$_2$CuO$_4$. Due to the long measuring times of approximately two months for such an investigation, the measurements of La$_2$CuO$_4$ were carried out only at 300 K.

3. Experimental results

La$_2$CuO$_4$ was investigated at 300 K and at pressures up to 226 kbar. The splitting of the (133) and (313) reflection was observed up to pressures of 41 kbar and showed no indication of a transformation from orthorhombic to tetragonal symmetry. This reflection group is shown in fig. 2. At higher pressures the NaF (220) reflection covers these reflections, due to the higher compressibility of the NaF. Fig. 3 shows the (200), (020), and (004) reflection of La$_2$CuO$_4$.

2. Experimental

La$_2$O$_3$ and CuO powders were mixed in appropriate portions to obtain La$_2$CuO$_4$ and pressed into pellets at a pressure of approximately 10 kbar. These pellets were heated in oxygen to 1323 K, followed by a heat treatment at 1223 K for two days. The pellets were cooled to room temperature in air.

Pr$_2$CuO$_4$ crystals were grown from a PbO-based flux. A mixture of the oxides in the proportions 0.09 PrO$_{3/2}$.0.37 PbO:0.54 CuO was heated in a Pt crucible to 1520 K in air, held 2 h, cooled to 1070 K at 7 K/h and then removed from the furnace. The solidified melt was tapped from the crucible and the cuprate crystals were separated from the CuO–PbO flux using very dilute acetic acid.

To perform high-pressure experiments the powdered specimen was mixed with a soft pressure transmitting medium (NaCl, NaF, ...) and filled into a 0.2 mm bore, which was drilled into an inconel gasket. The gasket was placed between the two diamonds of a high-pressure cell [14], which permits

Fig. 1. (a) La$_2$CuO$_4$ (K$_2$NiF$_4$ structure). (b) Pr$_2$CuO$_4$ (Nd$_2$CuO$_4$ structure).

Fig. 2. (113)/(313) reflections of La$_2$CuO$_4$ at several pressures.
the preservation of the orthorhombic structure of \( \text{La}_2\text{CuO}_4 \) up to 226 kbar. Figs. 4 and 5 show the volume dependence and the \( c/a \)-ratio as a function of pressure, which were calculated from the experimental data.

To illustrate the experimental results for \( \text{Pr}_2\text{CuO}_4 \), fig. 6 shows the measured intensities for the \( \text{Pr}_2\text{CuO}_4 \) (200)/(101) reflections at several pressures up to 255 kbar. The \( \text{Pr}_2\text{CuO}_4 \) (200) reflection shows no splitting, indicating the preservation of the tetragonal structure. The analysis of this peak is made difficult by the neighbourhood of the inconel (111) reflection at 19.8°, which gains intensity and broadens with increasing pressure due to the experimental setup. In addition, the \( \text{Pr}_2\text{CuO}_4 \) (006) reflection may

Fig. 4. Volume dependence of \( \text{La}_2\text{CuO}_4 \) as a function of pressure at 300 K (×).

Fig. 5. \( c/a \) ratio of \( \text{La}_2\text{CuO}_4 \) as a function of pressure at 300 K (×).

The width of the split (200)–(020) reflection was observed up to 226 kbar. The single peak of the (004) reflections shows just a slight broadening due to uniaxial pressure components. Thus, the nearly constant width of the (200)–(020) reflection indicates
overlap with the Pr$_2$CuO$_4$ (200) reflection at 140–180 kbar. Thus, we did not include this reflection at that pressure range in our analysis.

At ambient pressure the Pr$_2$CuO$_4$ (200) reflection overlaps with the NaCl (220) reflection, but already at 60 kbar these two reflections are separated due to the high compressibility of the soft NaCl.

The Pr$_2$CuO$_4$ (101) reflection shows no splitting in the whole investigated pressure range. The broadening at 255 kbar is caused by uniaxial pressure components, that were noticeable in this experimental run. This makes it also difficult to determine the exact position of the Pr$_2$CuO$_4$ (103)/(110) reflections shown in fig. 7 at 255 kbar. But observing the positions of the two reflections with increasing pressure up to 180 kbar allows an obvious interpretation of the measured spectrum at 255 kbar. The (103)/(110) reflections form a double peak structure at ambient pressure, including a small NaCl (200) reflection. At 60 kbar the NaCl (200) reflection is clearly separated. With increasing pressure the two reflections Pr$_2$CuO$_4$ (103)/(110) approach each other, as the (103) reflection moves faster than the
La$_2$CuO$_4$ is closely related to the perovskite structure. In this material perovskite layers with the general formula (ABX$_3$) alternate with rock salt layers (AX) [17]. Within experimental resolution, this material is uniformly compressed on the application of high pressure. In contrast, Pr$_2$CuO$_4$ shows a strong anisotropy in the reduction of the lattice parameters with increasing pressure. Considering the structures of both materials this must be a consequence of the degenerated oxygen octahedra in Pr$_2$CuO$_4$, since in this material the oxygen atoms are arranged in oxygen and Cu–O layers only.

To evaluate the dependence of the lattice parameters under pressure, the lattice parameter $g(P)$ is fitted by the expression

$$g(P) = g_0 + \beta_g g_0 P + \delta g_0 P^2$$

(with $g_0 = g$ at ambient pressure). This gives the linear compressibility $\beta_g$, which is normalized and thus independent of the size of the lattice parameter $g$. For orthorhombic materials, the three linear compressibilities are $\beta_a$, $\beta_b$ and $\beta_c$. The parameter $\delta g$ indicates the change of the linear compressibility with increasing pressure. Table 1 gives the calculated linear compressibilities for Pr$_2$CuO$_4$ and La$_2$CuO$_4$.

Within experimental resolution the dependences on pressure of $a$- and $b$-lattice parameters are essentially the same for La$_2$CuO$_4$ and Pr$_2$CuO$_4$. The only clear change was observed for the $c$-axis lattice parameter, with a linear compressibility for Pr$_2$CuO$_4$ being twice the value of La$_2$CuO$_4$. These different compressibilities in the $c$-direction are reflected in the bulk moduli, which have been calculated using the Birch equation of state [18]. La$_2$CuO$_4$ has a bulk modulus of $B = 1815 \pm 100$ kbar with a slope $B' = 5.6$, whereas Pr$_2$CuO$_4$ is more compressible with a bulk

| Material     | $\beta_a$ (kbar$^{-1}$) | $\beta_b$ (kbar$^{-1}$) | $\beta_c$ (kbar$^{-1}$) |
|--------------|------------------------|------------------------|------------------------|
| La$_2$CuO$_4$| $1.7 \times 10^{-4}$   | $2.0 \times 10^{-4}$   | $1.6 \times 10^{-4}$   |
| Pr$_2$CuO$_4$| $1.6 \times 10^{-4}$   | $1.6 \times 10^{-4}$   | $3.0 \times 10^{-4}$   |

Figs. 8 and 9 show the volume and the $c/a$ ratio of Pr$_2$CuO$_4$ versus pressure. There is no indication of any transformation in the investigated pressure range. The $c/a$ ratio decreases with increasing pressure, indicating a preferential $c$-axis decrease under pressure.
modulus of $B = 1600 \pm 100$ kbar and with a slope of $B' = 3.8$.

Regarding the structure of the high-$T_c$ materials, the Cu–O planes are a common feature. If these planes are mainly responsible for the low compressibility of $La_2CuO_4$ and $Pr_2CuO_4$ in the $a$, $b$-direction, there should be similar linear compressibilities $\beta_a$ and $\beta_b$ for all high-$T_c$ materials containing such Cu–O planes. We estimated the linear compressibilities for five high-$T_c$ materials using experimental results, which were previously published [9–11,13,19]. The obtained values are shown in table 2. For $YBa_2Cu_3O_7$ and $EuBa_2Cu_3O_7$ the calculation of the linear compressibilities is complicated by the ambiguity of the experimental results. The $c$-axis lattice parameter of these materials is nearly exactly 3 times bigger than the $b$-axis lattice parameter, resulting in overlapping X-ray reflections. Thus it is in principle not possible to distinguish between a preferential $c$-axis or $b$-axis decrease under high pressure, using powder diffraction techniques [9]. The results of the investigations of $La_2CuO_4$ and $Pr_2CuO_4$ suggest a preferential $c$-axis decrease under pressure. X-ray investigations of single crystals of $YBa_2Cu_3O_7$ showed also a preferential $c$-axis decrease under high pressure [20]. Thus the values of the linear compressibilities of $YBa_2Cu_3O_7$ and $EuBa_2Cu_3O_7$ have been calculated, assuming a preferential $c$-axis decrease under pressure. For all materials the linear compressibilities for the $a$- and $b$-lattice parameters are in the same range as for $La_2CuO_4$ and $Pr_2CuO_4$.

The results of high pressure investigations of $La_2CuO_4$ and $Pr_2CuO_4$ suggest a destabilisation of high-$T_c$ superconductors in the $c$-axis direction by degenerated oxygen octahedra and additional intercalated layers or structural elements. The stability in the $a$- and $b$-direction is ensured by the Cu–O planes, which gives similar linear compressibilities in these directions.

**Acknowledgement**

We like to thank D. Schiferl and S. Johnson for sharing with us the results of their powder X-ray measurements at high pressures on $Pr_2CuO_4$, which initialized our own investigations.

**References**

[1] R. Saez Puche, M. Norton and W.S. Glaunsinger, Mater. Res. Bull. 17 (1982) 1523.
[2] J.G. Bednorz and K.A. Müller, Z. Phys. B 64 (1986) 189.
[3] R.M. Fleming, B. Batlogg, R. Cava and E.A. Rietman, Phys. Rev. B 35 (1987) 7203.
[4] J.M. Tarascon, L.H. Greene, W.R. McKinnon, G.W. Hull and T.H. Geballe, Science 235 (1987) 1373.
[5] J. Beille, B. Chevalier, G. Demazeau, F. Deslandes, J. Etourneau, O. Laborde, C. Michel, P. Lejay, J. Provost, B. Raveau, A. Sulpice, J.L. Tholence and R. Tournier, Physica B 146 (1987) 307.
[6] J.D. Jorgensen, B. Dabrowski, Shiyiu Pei, D.G. Hinks, L. Soderholm, B. Morosin, J.E. Shirber, E.L. Venturini and D.S. Ginley, Phys. Rev. B 38 (1988) 11337.
[7] K.K. Singh, P. Ganguly and C.N.R. Rao, Mater. Res. Bull. 17 (1982) 493.
[8] H.K. Müller-Buschbaum and W. Wollschläger, Z. Anorg. Allg. Chem. 414 (1975) 76.
[9] N. Terada, H. Ihara, M. Hirabayashi, K. Senzaki, Y. Kimura, K. Murata, M. Tokumoto, O. Shimomura and T. Kikegawa, Japan. J. Appl. Phys. 26 (1987) L510.
[10] W.H. Fietz, M.R. Dietrich and J. Ecke, Z. Phys. B 69 (1987) 17.
[11] R. Moret, A.I. Goldman and A. Moodenbaugh, Phys. Rev. B 37 (1987) 7867.
[12] N. Terada, H. Ihara, M. Jo, M. Hirabayashi, K. Murata, H. Oyanagi, R. Sugise, O. Shimomura and T. Kikegawa, Physica C 153–155 (1988) 976.
[13] J.S. Olsen, S. Steenstrup, I. Johanssen and L. Gerward, Z. Phys. B 72 (1988) 165.
[14] R. Keller and W.B. Holzapfel, Rev. Sci. Instrum. 48 (1977) 517.
[15] W.H. Fietz, Report KfK 4482, Kernforschungszentrum Karlsruhe, FRG (1988).
[16] R.A. Forman, G.J. Piermarini, J.D. Barnett and S. Block, Science 176 (1972) 284.

[17] J.M. Longo and P.M. Raccah, J. Solid State Chem. 6 (1973) 526.
[18] F. Birch, Phys. Rev. 71 (1947) 809.
[19] M.R. Dietrich, W.H. Fietz, J. Ecke and C. Politis, Japan. J. Appl. Phys. 26, Suppl. 26-3 (1987) 1113.
[20] I.V. Aleksandriov, A.F. Goncharov and S.M. Stishov, Pis'ma Zh. Eksp. Teor. Fiz. 47 (1988) 357.