UC Irvine

UC Irvine Previously Published Works

Title

X-ray investigations of La₂CuO₄ and Pr₂CuO₄ under high pressure

Permalink

<https://escholarship.org/uc/item/1zg901r0>

Journal

Physics Letters A, 142(4-5)

ISSN

0375-9601

Authors

Fietz, WH
Wassilew, CA
Ewert, D
[et al.](#)

Publication Date

1989-12-11

DOI

10.1016/0375-9601(89)90334-4

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, availalbe at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

X-RAY INVESTIGATIONS OF La_2CuO_4 AND Pr_2CuO_4 UNDER HIGH PRESSURE**W.H. FIETZ, C.A. WASSILEW, D. EWERT, M.R. DIETRICH, H. WÜHL***Kernforschungszentrum Karlsruhe and Universität Karlsruhe, Postfach 3640, D-7500 Karlsruhe, FRG***D. HOCHHEIMER***Department of Physics, Colorado State University, Fort Collins, CO 80523, USA*

and

Z. FISK*Los Alamos National Laboratory, P-10, Los Alamos, NM 87545, USA*

Received 24 February 1989; revised manuscript received 2 October 1989; accepted for publication 10 October 1989

Communicated by D. Bloch

X-ray investigations of Pr_2CuO_4 and La_2CuO_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 La_2CuO_4 the lattice parameter reduction is isotropic with increasing pressure, but the lattice parameters of Pr_2CuO_4 are found to behave anisotropic, as the c -axis decreases faster than the a -axis. La_2CuO_4 has a bulk modulus of 1850 kbar at 300 K, whereas Pr_2CuO_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 2.0×10^{-4} 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

La_2CuO_4 has the K_2NiF_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 La_2CuO_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 La_2CuO_4 may also be induced by doping with excess oxygen, which ends in the formula $\text{La}_2\text{CuO}_{4+\delta}$ [5,6]. For a more meaningful

comparison of La_2CuO_4 with the non-superconducting Pr_2CuO_4 we decided to investigate the undoped and thus non-superconducting La_2CuO_4 rather than the doped La_2CuO_4 .

Pr_2CuO_4 has a Nd_2CuO_4 structure [7], which is closely related to the K_2NiF_4 structure. The structure of Pr_2CuO_4 is shown in fig. 1b. The materials crystallizing in the Nd_2CuO_4 structure are tetragonal. The striking difference between the structures of La_2CuO_4 and Pr_2CuO_4 is the location of the oxygen O(II) site [8]. These oxygen atoms are marked in fig. 1. In La_2CuO_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 O(II) site, the Cu-atoms have a square planar environment in Pr_2CuO_4 .

The structural investigation of these two materials may give a clue to the observed anisotropic pressure

Fig. 1. (a) La_2CuO_4 (K_2NiF_4 structure). (b) Pr_2CuO_4 (Nd_2CuO_4 structure).

dependence of the lattice parameters of high- T_c materials [9–13].

2. Experimental

La_2O_3 and CuO powders were mixed in appropriate portions to obtain La_2CuO_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_2CuO_4 crystals were grown from a PbO -based flux. A mixture of the oxides in the proportions $0.09 \text{ Pr}_{0.3/2} : 0.37 \text{ PbO} : 0.54 \text{ CuO}$ 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

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_2CuO_4 . Due to the long measuring times of approximately two months for such an investigation, the measurements of La_2CuO_4 were carried out only at 300 K.

3. Experimental results

La_2CuO_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_2CuO_4 .

Fig. 2. (113)/(313) reflections of La_2CuO_4 at several pressures.

Fig. 3. (020)/(200) and (004) reflections of La_2CuO_4 at several pressures.

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

the preservation of the orthorhombic structure of La_2CuO_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 Pr_2CuO_4 , fig. 6 shows the measured intensities for the Pr_2CuO_4 (200)/(101) reflections at several pressures up to 255 kbar. The Pr_2CuO_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 Pr_2CuO_4 (006) reflection may

Fig. 4. Volume dependence of La_2CuO_4 as a function of pressure at 300 K ($\times$).

Fig. 5. c/a ratio of La_2CuO_4 as a function of pressure at 300 K ($\times$).

Fig. 6. (101) and (200) reflections of Pr_2CuO_4 at several pressures.

overlap with the Pr_2CuO_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_2CuO_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_2CuO_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_2CuO_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

Fig. 7. (103) and (110) reflections of Pr_2CuO_4 at several pressures.

clearly separated. With increasing pressure the two reflections Pr_2CuO_4 (103)/(110) approach each other, as the (103) reflection moves faster than the

Fig. 8. Volume dependence of Pr_2CuO_4 as a function of pressure at 300 K ($\times$) and 30 K ($\square$).

Fig. 9. c/a ratio of Pr_2CuO_4 as a function of pressure at 300 K ($\times$).

(110) reflection. At 180 kbar these two reflections form a single peak. Therefore the c -lattice parameter shows a stronger decrease under pressure than the a -lattice parameter. We extrapolated the decrease of the a - and c -lattice parameter up to pressures of 255 kbar by using the values determined up to 180 kbar. The extrapolated reflection positions are marked in fig. 7 at 255 kbar. They are in good agreement with the shape of the double peak.

Figs. 8 and 9 show the volume and the c/a ratio of Pr_2CuO_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.

4. Discussion

La_2CuO_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_2CuO_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_2CuO_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

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

(with $g_0 = g$ at ambient pressure). This gives the linear compressibility β_g , which is normalized and thus independent of the size of the lattice parameter g . For orthorhombic materials, the three linear compressibilities are β_a , β_b and β_c . The parameter δ_g indicates the change of the linear compressibility with increasing pressure. Table 1 gives the calculated linear compressibilities for Pr_2CuO_4 and La_2CuO_4 .

Within experimental resolution the dependences on pressure of a - and b -lattice parameters are essentially the same for La_2CuO_4 and Pr_2CuO_4 . The only clear change was observed for the c -axis lattice parameter, with a linear compressibility for Pr_2CuO_4 being twice the value of La_2CuO_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_2CuO_4 has a bulk modulus of $B = 1815 \pm 100$ kbar with a slope $B' = 5.6$, whereas Pr_2CuO_4 is more compressible with a bulk

Table 1
Linear compressibilities of La_2CuO_4 and Pr_2CuO_4 at 300 K.

Material	β_a (kbar $^{-1}$)	β_b (kbar $^{-1}$)	β_c (kbar $^{-1}$)
La_2CuO_4	1.7×10^{-4}	2.0×10^{-4}	1.6×10^{-4}
Pr_2CuO_4	1.6×10^{-4}	1.6×10^{-4}	3.0×10^{-4}

Table 2

Linear compressibilities of several high- T_c superconductors.

Material	Reference	β_a (kbar $^{-1}$)	β_b (kbar $^{-1}$)	β_c (kbar $^{-1}$)
La _{1.7} Ba _{0.3} CuO ₄	[11]	2.0×10^{-4}	2.0×10^{-4}	1.7×10^{-4}
La _{1.8} Sr _{0.2} CuO ₄	[19]	1.7×10^{-4}	1.7×10^{-4}	2.3×10^{-4}
La _{1.4} Sr _{0.6} CuO ₄	[9]	1.9×10^{-4}	1.9×10^{-4}	2.3×10^{-4}
YBa ₂ Cu ₃ O ₇	[10]	1.8×10^{-4}	1.6×10^{-4}	2.3×10^{-4}
EuBa ₂ Cu ₃ O ₇	[13]	1.5×10^{-4}	1.8×10^{-4}	2.5×10^{-4}

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 La₂CuO₄ and Pr₂CuO₄ in the a -, b -direction, there should be similar linear compressibilities β_a and β_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 YBa₂Cu₃O₇ and EuBa₂Cu₃O₇ 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 La₂CuO₄ and Pr₂CuO₄ suggest a preferential c -axis decrease under pressure. X-ray investigations of single crystals of YBa₂Cu₃O₇ showed also a preferential c -axis decrease under high pressure [20]. Thus the values of the linear compressibilities of YBa₂Cu₃O₇ and EuBa₂Cu₃O₇ 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 La₂CuO₄ and Pr₂CuO₄.

The results of high pressure investigations of La₂CuO₄ and Pr₂CuO₄ 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 Pr₂CuO₄, 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, Shiyu 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. Raccach, J. Solid State Chem. 6 (1973) 526.
- [18] F. Birch, Phys. Rev. 71 (1947) 809.
- [19] M.R. Dietrich, W.H. Fietz, J. Ecker 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.