

SUPERCONDUCTIVITY AT 108 K IN $\text{YBa}_2\text{Cu}_4\text{O}_8$ AT PRESSURES UP TO 12 GPa

E.N. VAN EENIGE, R. GRIESSEN and R.J. WIJNGAARDEN

Department of Physics and Astronomy of the Free University, 1081 HV Amsterdam, The Netherlands

J. KARPINSKI, E. KALDIS, S. RUSIECKI and E. JILEK

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland

Received 11 May 1990

Resistive measurements in a cryogenic diamond anvil cell show that the T_c of $\text{YBa}_2\text{Cu}_4\text{O}_8$ can be increased by almost 30 K by applying a pressure of 12 GPa. The pressure derivative is, however, not constant. At $p \geq 5$ GPa, $dT_c/dp \approx 5$ K/GPa. At higher pressures dT_c/dp decreases gradually and T_c saturates at ~ 108 K. This behaviour is reproduced by a phenomenological model where T_c depends only on the number of holes in the CuO_2 planes.

1. Introduction

Soon after the discovery of superconductivity around 30 K in La–Ba–Cu–O by Bednorz and Müller [1], Chu et al. [2] showed that the T_c of $\text{La}_{0.8}\text{Ba}_{0.2}\text{CuO}_{3-\delta}$ could be increased to above 40 K by application of 1.5 GPa hydrostatic pressure. The pressure derivative $dT_c/dp = 6.1$ K/GPa was the largest ever observed in a superconductor. This large influence of pressure led to the idea of replacing La by a smaller atom, Y, in order to produce a “chemical” internal pressure. This resulted in the discovery of $\text{YBa}_2\text{Cu}_3\text{O}_7$ by Wu et al. [3]. The relevance of high-pressure experiments stimulated a large experimental activity from which the following trend emerged. The relative volume dependence $\ln T_c / \ln V$ of superconductors with a large T_c is much smaller in absolute value than that of high- T_c superconductors with low transition temperatures such as $\text{La}_2\text{CuO}_{4+\delta}$ and $(\text{La, Ba})_2\text{CuO}_4$ [4]. Possible origins of this trend have been discussed by Griessen [5], Wijngaarden and Griessen [4] and Murayama et al. [6].

In 1989, Bucher et al. [7] found a remarkably large pressure derivative $dT_c/dp = 5.5$ K/GPa in $\text{YBa}_2\text{Cu}_4\text{O}_8$ (with $T_c = 80$ K) for pressures up to 1.3 GPa. This pressure derivative is almost an order of magnitude higher than that of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The 124-

compound is thus rather unique and it is interesting to investigate its behaviour under much higher pressures. In this article we show that T_c may be increased by almost 30 K by application of 12 GPa by means of a diamond anvil cell.

2. Sample preparation

The first synthesis of bulk $\text{YBa}_2\text{Cu}_4\text{O}_8$ was achieved under high oxygen pressure by Karpinski et al. [8]. The high phase purity of the material was subsequently demonstrated by means of X-ray and neutron diffraction by Fischer et al. [9].

The ceramic material used in this work was also synthesized in a high temperature two-chamber autoclave [10]. A stoichiometric mixture of fine grained $\text{YBa}_2\text{Cu}_3\text{O}_7$ and CuO resulting from the decomposition of oxalates was heated to 980°C under 21 MPa oxygen for 30 h and then slowly cooled down at a rate of $5^\circ\text{C}/\text{min}$. From high sensitivity volumetric oxygen analysis [11] it is concluded that the material is stoichiometric with $\text{YBa}_2\text{Cu}_4\text{O}_{7.986 \pm 0.001}$. The T_c of bulk ceramic material is 80 K and thus similar to that of two-phased thin films investigated earlier by Kapitulnik [12]. The lack of twinning in $\text{YBa}_2\text{Cu}_4\text{O}_8$ makes it possible to accurately determine the a – b anisotropy in single crystals by means

of X-ray scattering. The orthorhombic lattice parameters are $a=3.8413$ Å, $b=3.8708$ Å and $c=27.240$ Å, with the double square planar chains in the b - c plane [13].

3. Experimental methods

A diamond anvil cell was used to apply pressures up to 12 GPa. The cell, which is entirely made of beryllium-copper, is mounted in an optical cryostat for optical access of the sample chamber. A heat exchanger incorporated in the body of the cell makes it possible to vary the temperature rapidly by flowing liquid helium. Pressure can be changed at any temperature by means of a knob at the top of the cryostat. The diamond anvil cell and optical cryostat are described elsewhere [14]. The samples used in this work consisted of a number of small pieces taken from a polycrystalline bulk sample prepared as described above. Each piece was checked for superconductivity by verifying that it levitated above a magnet at 77 K.

The pressure-chamber is schematically illustrated in fig. 1. The gasket is made of a stainless steel foil (T301, thickness ~ 200 μm) with a hole (diameter ~ 300 μm) as sample chamber. Six gold wires (diameter 25 μm) are laid onto the bottom diamond in such a way that after placing the gasket on top of them, they just reach the sample chamber. The insulation between gasket and wires consists of epoxy reinforced with Al_2O_3 -powder (grain size ~ 0.05 μm) and a 7 μm -thick kapton foil. Six wires are mounted (instead of four) so as to be able to select the best configuration for four-point resistivity measurements. A number of leads greater than the strict minimum makes it also possible to proceed with an experimental run even when one or two leads are cut at the diamond edges during pressurization. The room temperature resistivity is typically 100 m Ω . It is somewhat larger than the value of expected from $\rho=300$ $\mu\Omega$ cm at room temperature. This is probably due to contact resistance between grains of the crunched sampled in the diamond anvil cell.

Pressure is determined using the fluorescence of several grains of ruby which are pressurized together with the sample. The calibration of Mao et al. [15] for the shift in frequency with pressure corrected for

the temperature dependence of the ruby [16] is used.

Temperature is measured by means of a standard platinum resistor ($R(273\text{ K})=100$ Ω) mounted in a copper ring which fits precisely around one of the diamonds. Due to the good thermal contact the hysteresis between cooling-down and warming-up measurements is at most a few tenths of a degree.

4. Results

The variation of T_c with pressure for four different samples is shown in fig. 2. At low pressures $dT_c/dp \cong 5$ K/GPa in good agreement with the data obtained by Bucher et al. [7] at pressures below 1.3 GPa, by Tallon and Lusk [17] on 7% Ca doped samples and very recently by Diederichs et al. on pure samples at pressures up to 2.6 GPa [18]. Agreement is also found with the results of susceptibility measurements in single crystals under high pressure by Chouteau et al. [19]. The consistency of the sets of data is interesting in itself as it shows that large dT_c/dp are observed with completely different experiment techniques (a beryllium-copper self-clamping cell with a mixture of n-pentane and isoamylalcohol as pressure medium in ref. [7] and a diamond anvil cell without pressure medium in the present work). At higher pressure (above 5 GPa) dT_c/dp decreases gradually with increasing pressure. Above 10 GPa it is comparable to dT_c/dp in $\text{YBa}_2\text{Cu}_3\text{O}_7$ [20]. The highest value observed in the course of this work was $T_c \cong 108$ K. This is slightly larger than the highest value reported so far for a Y-Ba-Cu-O sample [4,21]. It is definitely the highest value ever observed for the $\text{YBa}_2\text{Cu}_4\text{O}_8$ system.

5. Discussion

In fig. 3 the pressure derivatives dT_c/dp (for $p \rightarrow 0$) of $\text{YBa}_2\text{Cu}_4\text{O}_8$ are compared to the many experimental data published so far for superconductors made of Y, Ba, Cu and O. Although relatively large dT_c/dp values have been reported in the literature for oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $T_c=20$ K, 45 K and ~ 70 K, the data in fig. 3 show clearly that dT_c/dp for stoichiometric $\text{YBa}_2\text{Cu}_4\text{O}_8$ is much larger compared to stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_7$. This is at

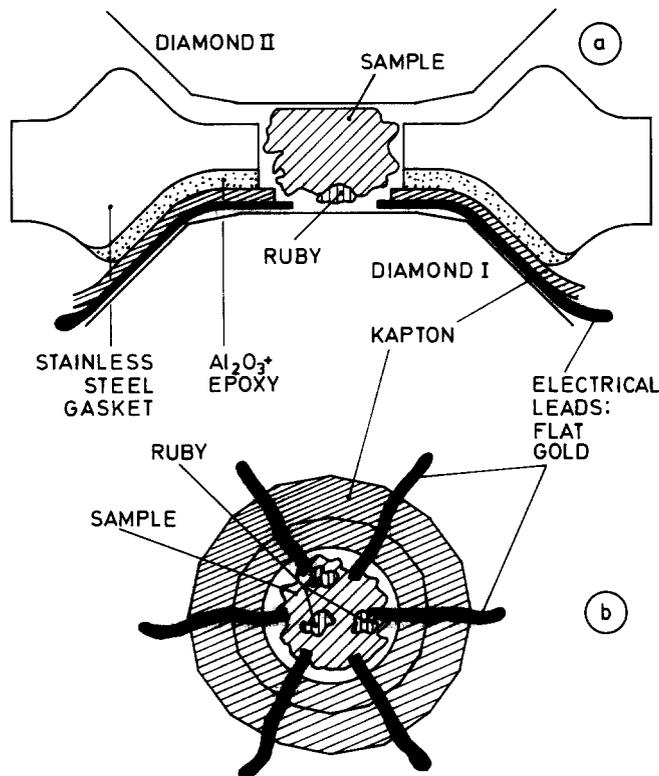


Fig. 1. Cross-section (a) and bottom-view (b) of the pressure chamber before compression. The gasket hole diameter is 300 μm .

first sight rather remarkable as the main structural difference between these two compounds is the presence of a double chain in $\text{YBa}_2\text{Cu}_4\text{O}_8$. In fact, the presence of a double chain in $\text{YBa}_2\text{Cu}_4\text{O}_8$ seems to be responsible for a peculiar behaviour of the lattice parameters under pressure. From table I one sees, as pointed out by Ludwig et al. [27], that $\text{YBa}_2\text{Cu}_4\text{O}_8$ is characterized by a large anisotropic pressure dependence of the a - and b -lattice spacings and a much larger linear compressibility along the c -axis. Most remarkable is also the large displacement of the apical oxygen (O_1) towards the CuO_2 plane under pressure determined by Kaldis et al. [28]. In a $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ sample (with $T_c = 20$ K), however, no such large relative displacement of the apical oxygen has been detected [29] although its pressure dependence ($dT_c/dp = 4$ K/GPa) is almost as large as that of $\text{YBa}_2\text{Cu}_4\text{O}_8$. The value of this observation is at present not clear [29] because this sample was tetragonal and a tetragonal sample is probably not in

equilibrium [33]. We still believe, therefore, that the contraction of the apical $\text{Cu}_2\text{-O}_1$ bond is most important in determining the increase in T_c . This is in agreement with the theoretical model of Bishop et al. [31] and the conclusions in a recent review by Müller [32].

In order to find an explanation for the saturation of T_c at high pressures shown in fig. 2 we discuss experimental results obtained recently for $\text{YBa}_2\text{Cu}_3\text{O}_x$. In fig. 4 we summarize relevant data by Cava et al. [33] for the oxygen dependence of T_c , the apical bond length $\text{Cu}_2\text{-O}_1$ and the c -axis. From a comparison of the curves in figs. 4(a) and 4(b) it is evident that the contraction of $\text{Cu}_2\text{-O}_1$ is directly related to the variation of T_c . From a calculation of the corresponding x -dependence of the bond valence sums V_j for the various anions and cations in $\text{YBa}_2\text{Cu}_3\text{O}_x$ Cava et al. also found that the concentration dependence of V_{Cu_2} was practically identical to that of T_c . It is thus reasonable to assume that T_c

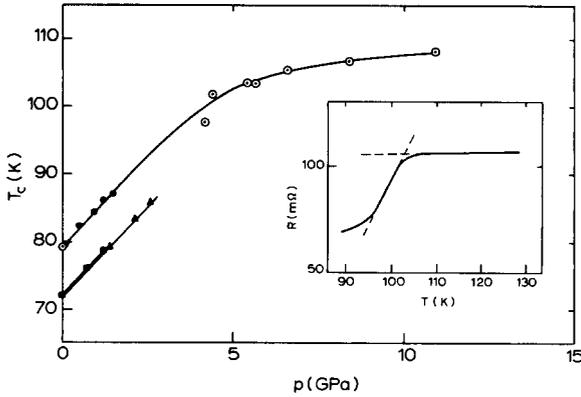


Fig. 2. Pressure dependence of $T_{c,\text{onset}}$ in $\text{YBa}_2\text{Cu}_4\text{O}_{7.986}$ as determined by Bucher et al. [7]: (●) polycrystalline sample, (■) single crystal, Diederichs et al. [18] (▲) and at high pressure (○) [this work]. The inset shows our $R(T)$ -curve measured for $p = 5.66$ GPa. The dashed lines indicate the way $T_{c,\text{onset}}$ was determined.

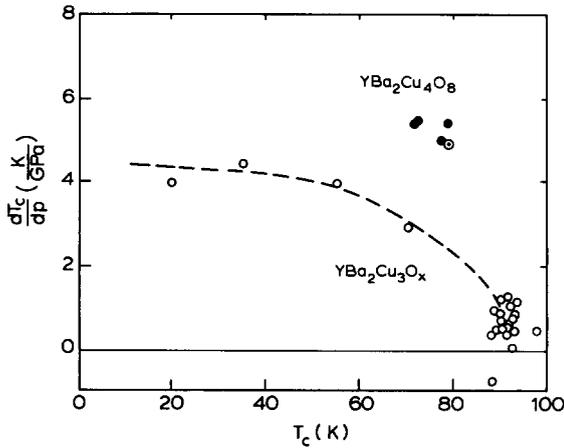


Fig. 3. Pressure derivatives vs. T_c curves for $\text{YBa}_2\text{Cu}_3\text{O}_x$ (○) and $\text{YBa}_2\text{Cu}_4\text{O}_8$ (●). For $\text{YBa}_2\text{Cu}_3\text{O}_x$ see refs. [4], [7], [22] and [23] and for $\text{YBa}_2\text{Cu}_4\text{O}_8$ refs. [7], [8], [24] and [25]. (⊙): the value obtained from an extrapolation to low pressure of our data in fig. 2. The line is a guide to the eye.

is mainly determined by the number n_h of holes in the CuO_2 planes. Most remarkable is that both ($\text{Cu}_2\text{-O}_1$) and the change in holes Δn_h exhibit a much more complicated behaviour than the c -axis, which apart from the abrupt change at the orthorhombic-tetragonal transition varies simply linearly with oxygen concentration. This observation, together with the

experimental data in fig. 5 (a) which show clearly that a saturation in T_c is also observed in substoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $x < 7$, suggest strongly a similarity in the behaviour of the number of holes Δn_h as a function of oxygen concentration and pressure. This can be expressed as

$$T_c(x, p) = \alpha(p) \cdot \Delta n_h(x, p). \quad (1)$$

At zero pressure $\alpha(0) = 92 \text{ K}/0.08 = 1150 \text{ K}$, and

$$T_c(x, 0) = 1150 \Delta n_h(x, 0) \equiv T_c(x). \quad (2)$$

Following the idea that a change in oxygen concentration produces an effect on T_c comparable to that of applying pressure as assumed in [28] and proved by [34], we make the simplifying assumption that

$$\Delta n_h(x, p) = \Delta n_h \left(\frac{x - x_0(p)}{7 - x_0(p)} (7 - x_0(p=0)) + x_0(p=0), 0 \right), \quad (3)$$

where $x_0(p)$ is the oxygen concentration at which T_c drops to zero, i.e. $x_0(p=0) \cong 6.35$. Equation (3) means that pressure causes a scaling of the concentration dependence of Δn_h . It is important to note here that eq. (3) does not imply that the oxygen stoichiometry changes under pressure. It simply means that there exists a relation between the influence of pressure on Δn_h and that of a change in oxygen stoichiometry on Δn_h . From eqs. (1) and (3) follows then that

$$\left. \frac{\partial T_c}{\partial x} \right|_p = \alpha(p) \Delta n'_h \frac{7 - x_0(p=0)}{7 - x_0(p)} \quad (4)$$

and

$$\left. \frac{\partial T_c}{\partial p} \right|_x = \frac{d\alpha}{dp} \Delta n_h + \alpha(p) \Delta n'_h \times \frac{(7 - x_0(p=0))(x - 7) dx_0}{(7 - x_0(p))^2 dp}, \quad (5)$$

where $\Delta n'_h$ is the derivative of the function Δn_h with respect to the variable $y = [(x - x_0(p)) / (7 - x_0(p))] \times (7 - x_0(p=0)) + x_0(p=0)$. At zero pressure eq. (5) reduces to

Table I

Pressure derivatives of the unit cell volume V , the lattice parameters a , b and c (the b -axis is taken along the direction of the chain(s)) and the distance between the apical oxygen O_1 and in-plane copper (Cu_2) and in-chain copper (Cu_1). Pressure is given in GPa. References are given within parentheses.

	$\text{YBa}_2\text{Cu}_3\text{O}_7$	$\text{YBa}_2\text{Cu}_4\text{O}_8$
$d \ln V / dp$	-6.4×10^{-3} [26]	-8.2×10^{-3} [27]
$d \ln a / dp$	-1.9×10^{-3} [26]	-2.8×10^{-3} [27]
$d \ln b / dp$	-1.8×10^{-3} [26]	-1.0×10^{-3} [27]
$d \ln c / dp$	-2.6×10^{-3} [26]	-4.5×10^{-3} [27]
$\frac{1}{(\text{Cu}_2-\text{O}_1)} \frac{d(\text{Cu}_2-\text{O}_1)}{dp}$		-21.5×10^{-3} [28]
$\frac{1}{(\text{Cu}_1-\text{O}_1)} \frac{d(\text{Cu}_1-\text{O}_1)}{dp}$		-37.3×10^{-3} [28]

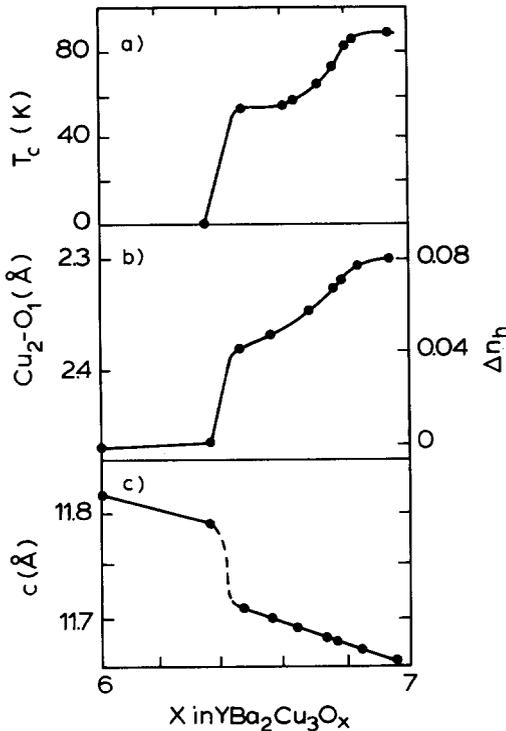


Fig. 4. Oxygen concentration dependence of T_c , the distance $\text{Cu}_2\text{-O}_1$ and the c -axis lattice parameter [33]. The scale for $\text{Cu}_2\text{-O}_1$ has been shown so as to show the similarity with the T_c vs. x -curve. The change Δn_h in the number of holes per Cu in the CuO_2 plane is essentially given by the same curve as $\text{Cu}_2\text{-O}_1$ (see figs. 8 and 15 in [33]). Δn_h is arbitrarily set equal to zero for $x=6$.

$$\left. \frac{\partial T_c}{\partial p} \right|_{x,p=0} = \frac{1}{\alpha(0)} \frac{d\alpha}{dp} T_c(x) + \frac{\partial T_c(x)}{\partial x} \left(\frac{x-7}{7-x_0(p=0)} \right) \frac{dx_0}{dp}. \quad (6)$$

For stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\partial T_c / \partial x \cong 0$, $T_c(x=7, 0) \cong 92$ K and $\partial T_c / \partial p \cong 0.5$ K/GPa [4,20] so that $(1/\alpha(0))d\alpha/dp = 5.4 \times 10^{-3}$ GPa $^{-1}$. For a substoichiometric sample $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ (with $T_c = 70$ K) Berman et al., [23] found $\partial T_c / \partial p \cong 3$ K/GPa which combined with $\partial T_c / \partial x$ ($x=6.74$, $p=0$) $\cong 210$ K leads to $dx_0/dp = -3.13 \times 10^{-2}$ GPa $^{-1}$. With these parameters (which have been determined in the limit $p \rightarrow 0$) we can write (using the definition in eq. (2)), that

$$T_c(x, p) = (1 + 0.0054p) T_c \left(\frac{0.65x + 0.2191p}{0.65 + 0.0313p} \right). \quad (7)$$

This means that $T_c(x, p)$ can easily be derived from the measured T_c versus x curve in fig. 4(a). The pressure dependence of T_c for samples with various oxygen contents obtained from eq.(7) and the T_c versus x curve in fig. 4(a) are compared to experimental data in fig. 5. The model reproduces nicely the main features of the data. It is gratifying that such a simple model can also reproduce the plateau around 70 K in $T_c(p)$ for the sample with $T_c(0) \cong 35$ K. The quantitative agreement is not as good for the samples with $T_c < 70$ K because of the large experimental uncertainties in the T_c versus x curve for $x < 6.4$ [29,30,33].

On the basis of the previous discussion of the pres-

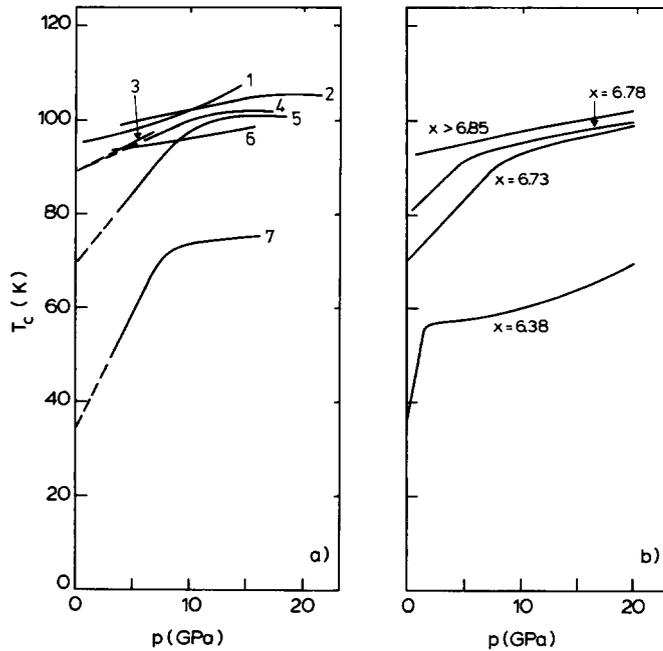


Fig. 5. Experimental (a) and calculated (b) pressure dependences of $T_{c,onset}$ in various $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples determined by resistivity measurements. The experimental data are from refs. [20] (curve 6), [21] (curve 1) and [23] (other curves). The curves in fig. 5(b) have been calculated by means of eq. (7) by using the $T_c = T_c(x)$ curve in fig. 4.

sure and oxygen concentration dependence of T_c in $\text{YBa}_2\text{Cu}_3\text{O}_x$, we arrive at the following interpretation of the $T_c(p)$ data in fig. 2. Although $\text{YBa}_2\text{Cu}_4\text{O}_8$ is a stoichiometric compound with a much higher oxygen stability than $\text{YBa}_2\text{Cu}_3\text{O}_7$ and its $T_c(x)$ has so far not been investigated in great detail, the similarity of the curves in figs. 2 and 5 suggests strongly that the saturation of the T_c of $\text{YBa}_2\text{Cu}_4\text{O}_8$ as a function of pressure is due to a saturation in the number of holes Δn_h with increasing pressure [34]. As an increase in Δn_h is directly related to the concentration of the $\text{Cu}_2\text{-O}_1$ bond length it would be highly desirable to carry out X-ray or neutron diffraction experiments to determine the behaviour of $(\text{Cu}_2\text{-O}_1)$ at pressures up to 15 GPa.

6. Conclusions

It has been shown that the T_c of $\text{YBa}_2\text{Cu}_4\text{O}_8$ can be increased up to 108 K by application of pressure up to 12 GPa. The similarity of the behaviour of

$\text{YBa}_2\text{Cu}_4\text{O}_8$ and stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_x$ under pressure and the similarity between a T_c change due to pressure and oxygen concentration in $\text{YBa}_2\text{Cu}_3\text{O}_x$ suggests that the saturation of T_c at pressures above ~ 5 GPa is related to a corresponding saturation in the number of holes in the CuO_2 planes of $\text{YBa}_2\text{Cu}_4\text{O}_8$.

Acknowledgements

We are grateful to D.M. de Leeuw and J.J. Scholtz for interesting discussions and to K. Heck for designing and implementing full computer control of the experimental equipment. We thank J.S. Schilling et al. for sending their results prior to publication. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) which is financially supported by NWO. The Zürich group is indebted to the Schulleitung of

the ETH and the Swiss National Fonds for financial support.

References

- [1] J.G. Bednorz and K.A. Müller, *Z.Phys.* B64 (1986) 189.
- [2] C.W. Chu, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang and Y.Q. Wang, *Phys. Rev. Lett.* 58 (1987) 405.
- [3] M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang and C.W. Chu, *Phys. Rev. Lett.* 58 (1987) 908.
- [4] R.J. Wijngaarden and R. Griessen, "High Pressure Studies" in: *Studies of High Temperature Superconductors*, vol. 2 ed. A.V. Narlikar (NOVA Science, New York, 1989) p. 29.
- [5] R. Griessen, *Phys. Rev.* B36 (1987) 5284.
- [6] C. Murayama, N. Nori, S. Yomo, J. Takagi, S. Uchida and Y. Tokura, *Nature* 339 (1989) 293.
- [7] B. Bucher, J. Karpinski, E. Kaldis and P. Wachter, *Physica C* 157 (1989) 478.
- [8] J. Karpinski, E. Kaldis, E. Jilek, S. Rusiecki and B. Bucher, *Nature* 336 (1988) 660.
- [9] P. Fischer, J. Karpinski, E. Kaldis, E. Jilek and S. Rusiecki, *Solid State Commun.* 69 (1989) 531.
- [10] J. Karpinski and E. Kaldis, *J. Cryst. Growth* 69 (1986) 47.
- [11] K. Conder, S. Rusiecki and E. Kaldis, *Mat. Res. Bull.* 24 (1989) 581.
- [12] A. Kapitulnik, *Physica C* 153 (1988) 520.
- [13] P. Bordet, J.L. Hodeau, R. Argoud, J. Muller, M. Marezio, J.C. Martinez, J.J. Prejean, J. Karpinski, E. Kaldis, S. Rusiecki and B. Bucher, *Physica C* 162-164 (1989) 524.
- [14] H. Hemmes, A. Driessen, J. Kos, F.A. Mul and R. Griessen, *Rev. Sci. Instrum.* 60 (1989) 474.
- [15] H.K. Mao, J. Xu and P.M. Bell, *J. Geophys. Res.* 91 (1986) 4673.
- [16] I.F. Silvera and R.J. Wijngaarden, *Rev. Sci. Instr.* 56 (1985) 121.
- [17] J.L. Tallon and J. Lusk, *Physica C* 167 (1990) 236.
- [18] J. Diederichs, W. Reith, B. Sundquist, K. Easterling, J. Niska and J.S. Schilling, private communication.
- [19] M. Chouteau, private communication.
- [20] A. Driessen, R. Griessen, N. Koeman, E. Salomons, R. Brouwer, D.G. de Groot, K. Heeck, H. Hemmes and J. Rector, *Phys. Rev.* B36 (1987) 5602.
- [21] M.W. McElfresh, M.B. Maple, K.N. Young and Z. Fisk, *Appl. Phys.* A45 (1988) 365.
- [22] R.J. Wijngaarden, *High Press. Res.* 3 (1990) 105.
- [23] I.V. Berman, N.B. Brandt, I.E. Graboi, A.R. Kaul, R.I. Kozlov, I.L. Romashkina, V.I. Sidorov and Khan Tsuiun, *Pis'ma Zh. Eksp. Teor. Fiz.* (1988) 634; *ibid.*, *JETP Lett.* 47 (1988) 733 and private communication.
- [24] B.M. Anderson, K.E. Easterling, B. Loberg, J. Niska and B. Sundqvist, *High Press. Res.* 3 (1990) 123.
- [25] B. Bucher, J. Karpinski, E. Kaldis, S. Rusiecki and P. Wachter, *High Press. Res.* 3 (1990) 108.
- [26] W.H. Fietz, M.R. Dietrich and J. Ecke, *Z. Phys.* B69 (1987) 17.
- [27] H.A. Ludwig, W.H. Fietz, M.R. Dietrich, H. Wühl, J. Karpinski, E. Kaldis and S. Rusiecki, *Physica C* 167 (1990) 335.
- [28] E. Kaldis, P. Fischer, A.W. Hewat, E.A. Hewat, J. Karpinski and S. Rusiecki, *Physica C* 159 (1989) 668.
- [29] E. Kaldis and J. Karpinski, *Europ. J. Solid State and Inorg. Chem.* no. 1-2 (1990), in press.
- [30] R.J. Cava, B. Batlogg, K.M. Rabe, E.A. Rietman, P.K. Gallagher and L.W. Rupp, *Physica C* 156 (1988) 523.
- [31] A.R. Bishop, R.L. Martin, K.A. Müller and Z. Tesanovic, *Z. Phys.* B76 (1989) 17.
- [32] K.A. Müller, *Z. Phys. B*, in print.
- [33] R.J. Cava, A.W. Hewat, E.A. Hewat, B. Batlogg, M. Marezio, K.M. Rabe, J.J. Krajewski, W.F. Peck and L.W. Rupp, *Physica C* 165 (1990) 419.
- [34] P. Allenspach, J. Mesot, U. Staub, A. Furrer, H. Blank, H. Mutka, C. Vettier, E. Kaldis, J. Karpinski and S. Rusiecki, to be published in *Europ. J. Solid State Chemistry*.