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Pressure dependence of T_c and H_{c2} of $CaLaBaCu_3O_7$ up to 50 GPa

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At $\partial \ln T_c/\partial p = 1.5\times 10^{-3}$ GPa^{-1}, the relative change of the superconducting critical temperature T_c with pressure p in $CaLaBaCu_3O_7$ is found to be smaller than in any other high-T_c compound. Even more remarkable is that this low value applies to the whole range from 0 to 50 GPa (with is the highest pressure ever reached in the investigation of T_c for any compound). Using measurements of the upper critical field H_{c2} (T, p) to 40 GPa, we deduce that (1) the charge carrier concentration is virtually unaffected by pressure, in striking contrast with e.g. $YBa_2Cu_4O_8$ and (2) that the net effect on T_c of the pressure induced changes of all other parameters is extremely small.

1. Introduction

Since the discovery of high-T_c superconductors by Bednorz and Müller [1] many theories, including modifications of the standard BCS-theory, have been put forward to explain the high values of their critical temperatures. Because a number of parameters of these theories are inherently affected by pressure, we have performed high pressure experiments. In this work we present experimental results on the interesting tetragonal compound $CaLaBaCu_3O_7$ up to 50 GPa. This is the largest pressure ever used for the investigation of the critical temperature of high-T_c superconductors. The data show that T_c is almost constant up to the highest pressure. This is a very remarkable result since the volume compression is $\Delta V/V \cong 25\%$. It is also unique among the high-T_c superconductors. In sharp contrast $YBa_2Cu_4O_8$, which has almost the same T_c, has a very large $\partial T_c/\partial p \cong 5$K/GPa at zero pressure, which leads to an increase to 108 K at 10 GPa followed by a small decrease up to 20 GPa [2,3]. After a discussion of the experimental technique, results on the pressure dependence of both the critical temperature and the upper critical field are presented. Since it is known from our own and other work that the charge carrier concentration is an important parameter for the prediction of T_c, we continue by presenting a calculation of the change of charge carrier concentration with pressure from our experimental data. Finally we discuss some of the consequences of our present findings.

2. Experimental technique

Samples were prepared using the mixed oxide route described by de Leeuw et al. [4]; the resulting material is isomorphic to tetragonal $YBa_2Cu_3O_{6+x}$ $(x<0.35)$ with the Ca ions at the Y site and the La and Ba ions located at the Ba site. The crystal structure is shown in fig. 1. From X-ray experiments [4] the zero-pressure lattice parameters were found to be: $a=0.38655$ nm and $c=1.16354$ nm. Both from X-ray and neutron diffraction experiments a superstructure is evident, suggesting an ordering of the oxygen in the planes marked A in fig. 1, combined with La/Ba ordering. The reason for this behaviour has not yet been clarified [5]. The pressure dependence of T_c and H_{c2} is measured by means of a specially designed [6] cryogenic diamond anvil cell which fits into the bore of a 12 T Thor-Cryogenic superconducting magnet together with an optical cryostat en-

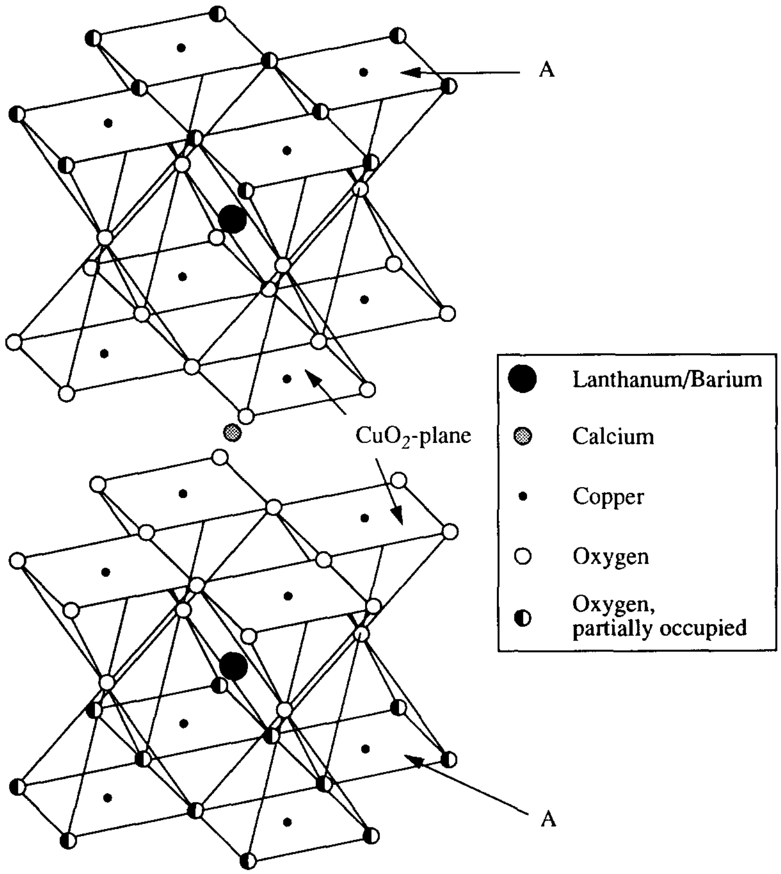

Fig. 1. Crystal structure of $CaLaBaCu_3O_7$. In the planes marked A only half of the oxygen sites are occupied, the distribution of occupied sites is random.

abling optical access to the sample space. The cell is made of non-magnetic stainless steel and the force generating mechanism is situated outside the magnet thus avoiding large mechanical components in the bore. The diamonds are 16 sided and single bevelled with a culet diameter of 800 μm. Pressure is measured by the R1 ruby fluorescence, using the pressure scale of Mao et al. [7], corrected for low temperature [8]. Several ruby chips were used, enabling the determination of pressure gradients. At 2 GPa the gradient over the full sample diameter was 5% and at 50 GPa it increased to 20%. Since we use the onset T_c and since $\partial T_c/\partial p$ is positive, the maximum pressure is the pressure used to plot the resistively determined T_c.

The temperature can be changed continuously down to 10 K by means of a continuous flow helium system directly mounted on the diamond anvil cell. Sweep rates are typically 1K/min. Above 30 K (relevant for the present work) a platinum thermometer, calibrated for magnetic fields, is used.

3. Pressure dependence of the critical temperature

To determine T_c, four-point resistivity measurements were done on the 400 μm diameter samples, using an insulated gasket and four gold wires pressed onto the sample, as described previously by van Eenige et al. [2]. To measure the very small resistances, a low frequency lock-in technique was used, which reverses the 1 mA measurement current every 0.25 s, thus also correcting for thermovoltages. The onset T_c, which is the T_c used here throughout, is determined from the tangents on the resistivity curve in the normal state and halfway down the transition, as shown in the inset of fig. 2.

In the main figure we show this onset critical temperature in zero magnetic field as a function of pressure. To check for irreversible behaviour the pressure was decreased twice (at 12.5 and 38.9 GPa), which is the main reason for the scatter of the data. Apart from the highest pressure point, the data follow a straight line with slope $\partial T_c/\partial p = +0.12 \pm 0.03$ K/GPa. This implies a relative slope of $\partial \ln T_c/\partial p = 1.5 \times 10^{-3}$ Gpa^{-1}, a very small value, three times smaller than for $YBa_2Cu_3O_7$ and forty times smaller than for $YBa_2Cu_4O_8$ [2]. Even in conventional superconductors the extremely small $\partial \ln T_c/\partial p$ is unequaled, particularly if the large pressure range is taken into account. The volume compression corresponding to 50 GPa is larger than 25% if we assume for (tetragonal) $CaLaBaCu_3O_7$ the same bulk modulus $B = 125$ GPa as for $YBa_2Cu_3O_6$, which is also tetragonal. This means that a large change in e.g. phonon frequencies and electronic overlap integrals is expected. This implies that according to certain theories a large change in T_c would be expected. For example in the BCS theory for superconductivity, where electrons are coupled through electron–phonon interaction, a simple formula for the critical temperature is

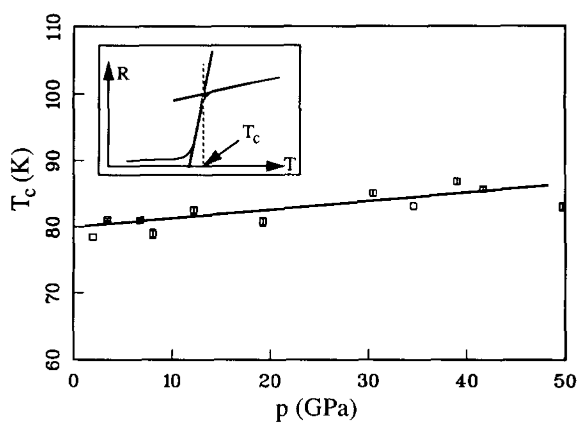

Fig. 2. Onset critical temperature, as defined in the text and shown in the inset, for $CaLaBaCu_3O_7$. Most of the scatter in the data was caused by lowering the pressure twice during this run. Error bars show the difference between cooling and heating. The line is a guide to the eye.

$$k_B T_c = \hbar \omega_p \exp\left[-\frac{1}{N(0)V}\right]. \quad (1)$$

Generally pressure will change the average phonon frequency ω_p, the density of states at the Fermi-surface $N(0)$ and (to a lesser extend) the electron–phonon interaction strength V. The net effect is, very generally, a significant decrease of T_c with pressure [9]. To take another example, in the RVB theory [10] a very simple T_c formula is

$$T_c \propto \delta \frac{t_\perp^2}{t_\parallel}. \quad (2)$$

Pressure increases the carrier concentration δ, as will be discussed from an experimental viewpoint later in this contribution; the in- and out- of-plane transfer integrals $t_\parallel$ and $t_\perp$ are expected to strongly increase as a function of pressure due to the increasing overlap of wavefunctions. Hence, as we have previously argued [11] ar large positive $\partial T_c/\partial p$ is expected from this theory.

4. Pressure dependence of the upper critical field

Since it is clear from the literature that there is presently no firm consensus on the definition of the upper critical field as measured resistively, we now briefly discuss why the onset T_c, as defined above, corresponds to the correct T_c and can be used to determine the upper critical field H_{c2}. Taking into account flux flow and flux creep phenomena, $R(T)$ curves in a magnetic field have been calculated by one of us [12]. From this work it is clear that the onset critical temperature measured resistively corresponds to the thermodynamical T_c. In the calculation mentioned, fluctuation conductivity was not taken into account, but our definition of T_c takes care of that since fluctuation effects play only a minor role for the resistivity below T_c. Secondly, in a very careful measurement at zero pressure on detwinned $YBa_2Cu_3O_7$ single crystals, Welp et al. [13] have compared the resistive transition in a magnetic field with the magnetization curves. From their resistive curves, we determined T_c as defined above and found that a nice agreement exists between T_c from resistivity and magnetization measurements (within $\sim$0.25 K).

To determine the upper critical field H_{c2} resistance was measured as a function of temperature in external fields of 0 T, 1 T, 4 T and 10 T. For each applied field H the onset of the resistive transition, found at a temperature T, defines the upper critical field H_{c2} $(T)=H$. In fig. 3 we show this temperature dependent upper critical field for various pressures. It is interesting to extrapolate H_{c2} at these high temperatures to the thermodynamically more relevant H_{c2} $(T=0)$. For this purpose we use the theory of Werthamer, Helfand and Hohenberg [14] (WHH), which is based on the BCS theory. The analysis does not depend critically on the use of the WHH theory. As discussed in ref. [3] approximately the same results are obtained using different methods for the calculation of H_{c2} $(T=0)$. The WHH theory contains the spin–orbit scattering parameter λ_{so}, which is unknown for $CaLaBaCu_3O_7$. Varying λ_{so} between zero and infinity will vary H_{c2} by about a factor of two. However, the relative change with pressure of H_{c2} is unaffected (we take λ_{so} to be pressure independent). As a rough estimate we take $\lambda_{so}=2$, which is van Bentum et al.'s [15] value for $La_{1.85}Sr_{0.15}CuO_4$. The result is shown in table 1 and fig. 4(a). The corresponding coherence length $\xi(0)$ can be calculated from the Ginzburg–Landau relation

$$\mu_0 H_{c2}(0)=\frac{\Phi_0}{2\pi\xi^2(0)}\,, \qquad (3)$$

where $\Phi_0=h/2e$ is the flux quantum. The result is

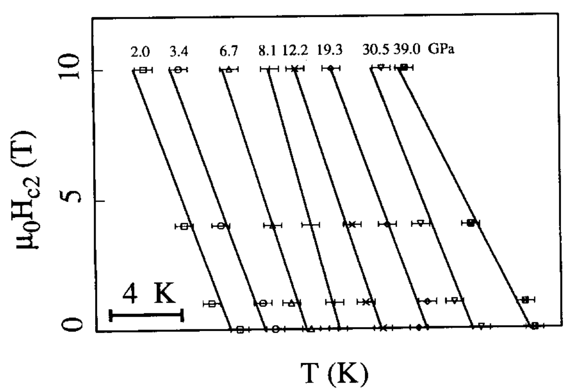

Fig. 3. H_{c2} as a function of temperature and pressure. To avoid crossing of lines we have arbitrarily translated the $\mu_0 H_{c2}(T)$ curves along the temperature axis. The actual values of T_c at zero field are given in fig. 2.

Table 1
Measured critical temperature $T_c(H=0)$ in zero applied magnetic field and the derivative of the upper critical field $\partial H_{c2}/\partial T$ at $T=T_c$, which was determined from a linear fit through the data of fig. 3. This linear fit intersects the temperature axis at T_c^*. The upper critical field at zero temperature $H_{c2}(0)$ is calculated from $\partial H_{c2}/\partial T$ and T_c^* using the WHH theory [14]

p GPa	$T_c(H=0)$ (K)	T_c^* (K)	$-\frac{\partial \mu_0 H_{c2}}{\partial T}$ (T/K)	$\mu_0 H_{c2}(0)$ (T)
1.83	78.45	77.91	1.9723	97.57
3.15	81.07	80.87	1.8573	95.62
6.91	81.02	80.71	2.3668	116.34
8.15	78.94	79.03	2.6603	124.56
12.45	82.49	82.40	2.1690	110.81
19.48	80.77	81.29	1.8731	96.81
30.53	85.05	84.51	1.8566	99.89
38.87	86.80	86.77	1.3574	77.80

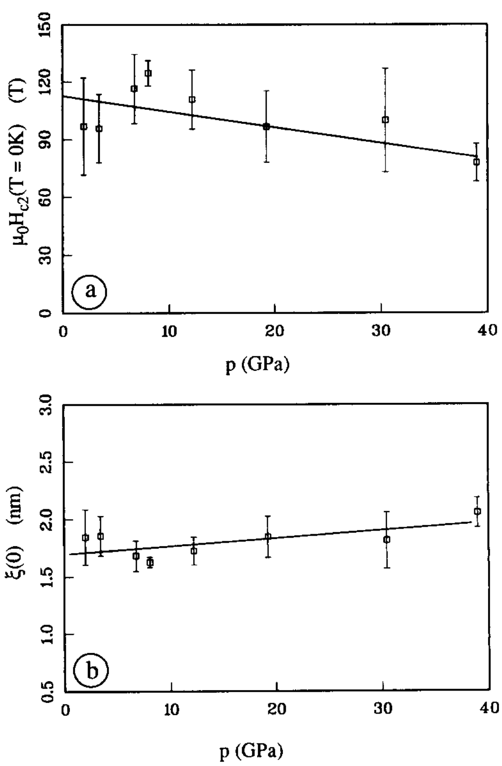

Fig. 4. (a) $H_{c2}(T=0)$ determined from the WHH theory with $\lambda_{so}=2$, (b) $\xi(T=0)$ determined from H_{c2} $(T=0)$ using eq. (3).

shown in fig. 4(b). Clearly both H_{c2} (0) and $\xi(0)$ vary very little with pressure.

The charge carrier concentration is an important parameter for the determination of T_c. From a large body of experimental data on substituted high-T_c superconductors it is empirically known that T_c follows approximately an inverted parabola i.e. $T_c = T_0 \{1-\beta(\delta-\delta_0)^2\}$ where δ is the number of holes per planar copper atom (i.e. in the layer marked "CuO_2-plane" in fig. 1) and $\beta \cong 60$ [16]. For a review on this relation see Shafer and Penney [17]. Among others, the T_c (p) behaviour will be influenced by the pressure dependence of δ, which can be derived [18] from the above measurement of H_{c2} as we will now show.

For a cylindrical Fermi surface [19] with radius k_F and height $2\pi/c$, where c is a lattice parameter, the Fermi velocity is given by

$$v_F = \frac{h}{m^*}\sqrt{\frac{cn}{2\pi}}, \tag{4}$$

with m^* the effective mass in the ab-plane and $n=N/V$ the charge carrier concentration per unit volume [20]. If N is the total number of charge carriers and N_{Cu} the total number of planar copper atoms, then $N=nV=\delta N_{Cu}$ or $\delta = nV/N_{Cu}$. Using the Brinkman and Rice relation $m^* \sim 1/\delta$ [21]; the uncertainty relation $\xi = \hbar/\Delta p \propto \hbar v_F/k_B T_c$ with ξ defined by eq. (3) and also eq. (4) we find [18]

$$\delta^3 \propto \frac{T_c{}^2 V}{cH_{c2}(0)}. \tag{5}$$

Within the framework of the BCS theory the exact value of the proportionality constant can be calculated. To find the relative change in charge carrier density, however, knowledge of this proportionality constant value is not necessary since eq. (5) implies

$$\frac{\partial \ln \delta}{\partial p} = -\frac{1}{3B} - \frac{1}{3}\frac{\partial \ln c}{\partial p} - \frac{1}{3}\frac{\partial \ln H_{c2}(0)}{\partial p} + \frac{2}{3}\frac{\partial \ln T_c}{\partial p}. \tag{6}$$

The bulk modulus $B = (-\partial \ln V/\partial p)^{-1}$ and $\partial \ln c/\partial p$ are assumed to have the same values as for $YBa_2Cu_3O_6$ which is structurally equivalent to $CaLaBeCu_3O_7$. Fietz et al. [22] find 125 GPa and 4×10^{-3} GPa^{-1}, respectively, from X-ray experiments under high pressure. The last two terms in eq. (6) are, of course, known from the present experiment. We find $\partial \ln \delta/\partial p = 0.0025$ GPa^{-1} or a change of 12.5% from zero pressure to our highest pressure of 50 GPa. This change is much smaller than that for e.g. $YBa_2Cu_4O_8$, where $\partial \ln \delta/\partial p = 0.045$ is nearly twenty times larger [3]! A possible explanation for the very small $\partial \ln \delta/\partial p$ in $CaLaBaCu_3O_7$ is that the structure is tetragonal. This implies that instead of long CuO-chains, there are only very short segments of CuO-chain, with random (but short) length and with a random distribution between "a-" and "b-" directions. The electrons in such a segment are highly localized and have such a high momentum that transfer from chains to planes is nearly impossible [23]. In agreement with this intuitive idea, electronic structure calculations by Gupta and Gupta [24] have shown that charge transfer from chains to planes is possible only in the case of long chains, which are not present in $CaLaBaCu_3O_7$.

We have thus explained why only a small change of T_c should be expected, based on carrier concentrations only. From our experiment it is clear that the net effect of the pressure induced change in all other factors on T_c is practically zero. At this point it is not clear whether there is an accidental cancellation, or whether T_c is indeed unaffected by changes in phonon-frequency, transfer integrals etc. Experiments to elucidate this question by exploring the behaviour of specific compounds under influence of chemical doping and pressure simultaneously are under way.

5. Conclusion

We have measured T_c and H_{c2} of $CaLabBaCu_3O_7$ to 50 GPa in a cryogenic diamond anvil cell which is situated in a 12 T superconducting magnet and found a remarkable small change of T_c with pressure, particularly if one realizes that the volume compression at 50 GPa is more than 25%. The small change of T_c is apparently caused by the fact that pressure induced charge transfer in this compound is very difficult and also by a cancellation or non-existence of the pressure induced change in other factors affecting T_c.

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