

PRESSURE DEPENDENCE OF THE T_c OF Bi-Ca-Sr-Cu-O UP TO 80 KBAR

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The superconducting transition temperature T_c of polycrystalline Bi-Ca-Sr-Cu-O ($T_c=92.4$ K) was measured by monitoring the electrical resistivity in a diamond anvil cell. T_c is found to decrease at a rate of $dT_c/dp=-0.16$ K/kbar up to 80 kbar. This is the first high temperature superconductor which shows a clear decrease of T_c with pressure. The pressure dependence is qualitatively explained in terms of a Hubbard-like model.

1. Introduction

Soon after the discovery of high temperature superconductivity in La-Ba-Cu-O [1], Chu et al. [2] reported that the superconducting temperature T_c of this compound could be increased by applying hydrostatic pressure. At a pressure of 14 kbar the T_c had increased from 32 K to 40 K. With a $dT_c/dp=0.64$ K/kbar the pressure of La-Ba-Cu-O is one of the largest measured so far.

In the Y-Ba-Cu-O superconductor a much higher $T_c=92$ K was found. The pressure dependence, however, is much smaller as follows from the measurements by Hor et al. [3] up to 19 kbar, by Driessen et al. up to 170 kbar [4], by Lotter and Wittig [5] up to 100 kbar and by Fietz et al. [6] up to 20 kbar.

In this paper we present our results for Bi-Ca-Sr-Cu-O with a T_c of 92.4 K.

2. Sample preparation

The sample was made by a standard solid state reaction technique from CaCO_3 , SrCO_3 , Bi_2O_3 and CuO. The powder ingredients were thoroughly mixed, pressed into pellets and heated at 800°C. Then the pellets were pulverized, mixed and again pressed into pellets. These were heated at 870°C and subse-

quently quenched in liquid nitrogen. Details of the sample preparation procedure will be published elsewhere [7]. At T_c the resistivity of our sample does not become zero. A rather broad tail extends to 4.2 K and even at that temperature the resistance is not completely zero. This is attributed to the existence of at least two phases in the sample, one superconducting and one non-superconducting. From the large diamagnetic response of the sample we conclude, however, that part of the sample volume is superconducting above liquid nitrogen temperature. The results presented here give therefore a true indication of the behaviour of the superconducting phase.

3. Experimental procedure

A diamond anvil cell was used to apply pressures up to 80 kbar. The cell and optical cryostat are similar to those described by Silvera and Wijngaarden [8] and will be described in detail elsewhere [9]. For the present work it is sufficient to mention that the body of our cell incorporates the heat exchanger of a continuous flow liquid helium or nitrogen system. This enables relatively rapid temperature sweeps over the whole operating range (1.5 to 300 K) of the diamond anvil cell. The cell is made of beryllium copper (Berylco 25) and is designed for a maximum

force of 3000 kgf on the diamonds. The samples used in this work consisted of a conglomerate of small grains taken from a polycrystalline bulk sample prepared as described above. These grains were separately checked for their superconducting properties by verifying that they levitated above a small magnet when immersed in liquid nitrogen.

The pressure chamber is schematically illustrated in fig. 1. Two flat copper wires are mounted on diamond I. These wires serve as contact leads to the sample and enable a semi-four point measurement of its resistivity. The superconducting transition temperature T_c is determined from the drop in the resistivity of the sample observed in temperature sweeps. On top of the copper wires sits an insulated gasket. The insulation consists of a layer of epoxy resin reinforced with Al_2O_3 (grain size $\sim 30 \mu\text{m}$) and a $25 \mu\text{m}$ thick kapton foil.

At pressures above ~ 6 kbar the room-temperature resistance of the sample was $\sim 200 \Omega$. This is attributed to contact resistance between the different grains and between grains and copper wires. Pressure was

determined using the fluorescence of several grains of ruby which were pressurized together with the sample. We used the calibration of Mao et al. [10] for the shift in frequency with pressure. We corrected for the temperature dependence of the ruby frequency by using the fit by McCumber and Sturge [11]. The temperature was determined with a standard platinum resistor [$R(273 \text{ K}) = 100 \Omega$].

4. Results

The resistance of the sample was measured using the four ends of the two copper wires (fig. 1) for a semi-four point d.c. measurement. Typical resistance was 200Ω at room-temperature. Even at 4.2 K the resistance of the sample did not become zero so that the superconducting transition was superimposed on a semiconductor-like background. We suggest that this is due to a mixture of two phases in the sample, one superconducting and one semiconducting. Using a fit to the low temperature part of the resistivity curve, we were able to extract the behaviour of the superconducting part of the sample. The result is plotted in fig. 2. The decrease in the normal resistivity above T_{co} is believed to arise from

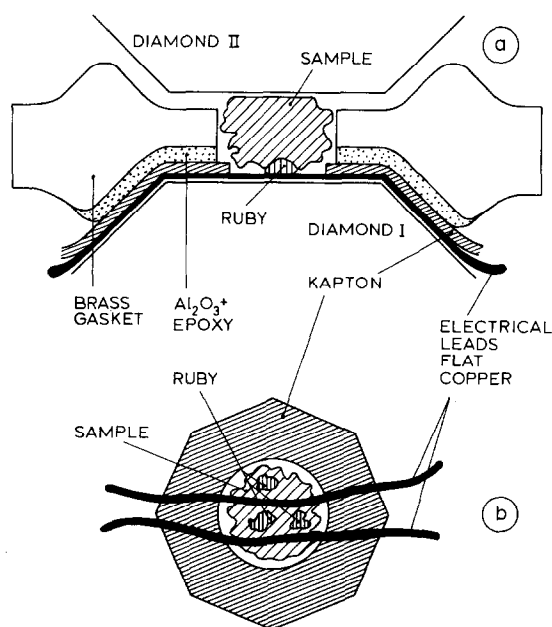


Fig. 1. Schematic cross section (a) and bottom view (b) of the sample containment chamber before compression. Note the four terminals for resistivity measurements and the ruby-grains for in situ pressure measurement. The diameter of the sample is $\sim 200 \mu\text{m}$.

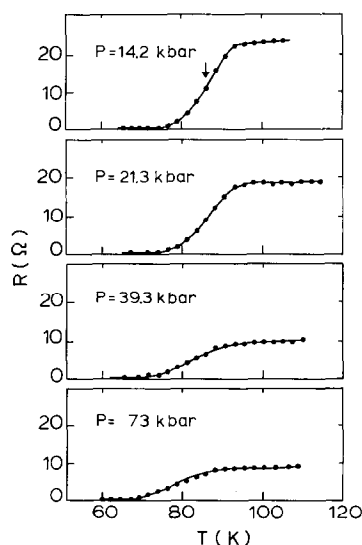


Fig. 2. Superconducting transition at different pressures as obtained from resistivity measurements after subtraction of the semiconducting background resistance.

the compression of the sample and the increase of the semiconducting background. Nearly no hysteresis was observed with respect to increasing or decreasing temperature scans. For the determination of T_c we define three points on the resistivity curve. T_m is the inflection point as indicated by an arrow in fig. 2. T_{co} is the onset temperature; it is the point of intersection of the tangent at the inflection point and the extrapolated behaviour above the transition, T_{cf} is the final temperature; it is the point of intersection of the tangent at the inflection point with the $R=0$ axis. These temperatures T_{co} , T_m and T_{cf} are plotted in fig. 3. This plot contains points taken with increasing as well as with decreasing temperature. At zero pressure we measured $T_{cf}=86.8$ K, $T_m=92.4$ K and $T_{co}=98.0$ K. These points were not included since they were taken in a separate experiment on the bulk sample before pulverization into grains. We note that T_c decreases roughly linearly with increasing pressure with a slope $dT_m/dp = -0.16$ K/kbar. The width of the transition increases, as was previously observed in $YBa_2Cu_3O_7$ samples [3,4]. During these measurements pressure was never decreased. The measurement could not be extended beyond 80 kbar because of short circuit of the contact leads to the sample.

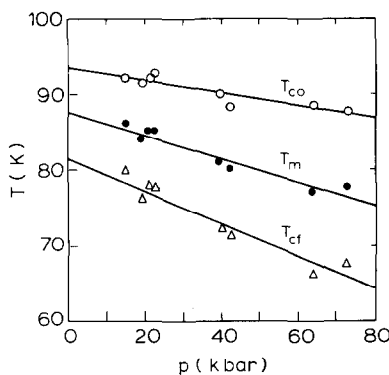


Fig. 3. Superconducting transition temperatures T_{co} (onset), T_m (inflection point) and T_{cf} (final) of Bi-Ca-Sr-Cu-O as a function of pressure, determined from electrical resistivity curves such as those of fig. 2.

5. Discussion

To obtain the volume dependence of T_c , needed for comparison with theoretical predictions, we use the relationship

$$\frac{d \ln T_c}{d \ln V} = - \frac{B d T_c}{T_c dp} \quad (1)$$

In fig. 4 we show a plot of $d \ln T_c / d \ln V$ versus T_c for a number of high temperature superconductors, including Bi-Ca-Sr-Cu-O. The bulk modulus B of Bi-Ca-Sr-Cu-O is assumed to have the same value as the bulk modulus of $YBa_2Cu_3O_7$, i.e. $B=1.7$ Mbar, as determined by Salomons et al. [12]. The consequences of the observed pressure effect for some theoretical models on high temperature superconductivity have been discussed by Griessen [13] and by Driessen et al. [4].

In this paper we will discuss some consequences of a model based on the Hubbard Hamiltonian

$$H = \sum_{i,j} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (2)$$

where U is the intra-atomic Coulomb energy integral

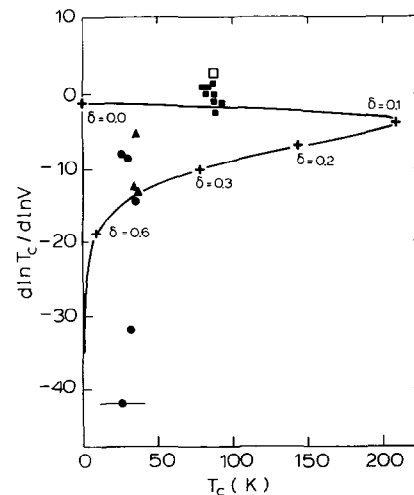


Fig. 4. Plot of $d \ln T_c / d \ln V$ versus T_c . The points represent measurements on various high- T_c superconductors: \bullet : La-(Ba)-Cu-O, \blacktriangle : La-Sr-Cu-O, \blacksquare : Y-Ba-Cu-O, \square : Bi-Ca-Sr-Cu-O. References to the measurements are given in ref. [13]. Also shown is a curve obtained from eqs. (3)-(5) as explained in the text with $t=0.5$ eV, $U=5$ eV, $d \ln U / d \ln V=0$, $d \ln t / d \ln V=-2$ and $d \ln \delta / d \ln V=1$. Indicated along this curve is the average number δ of holes per site.

and t_{ij} is the hopping integral between sites i and j for charge carriers, which for simplicity is taken to be non-zero and equal to t for nearest-neighbour hops only. For doped superconductors, e.g. La_2CuO_4 doped with Ba or Sr or $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $x > 6.5$ the superconducting transition temperature depends not only on t and U but also on the average number δ of holes per site. From dimensional consideration one expects [14] that

$$k_B T_c = \frac{t^2}{U} f\left(\frac{t}{U}, \delta\right). \quad (3)$$

Bandstructure calculations on La-Ba-Cu-O [15,16], La-Sr-Cu-O [15,16] and Y-Ba-Cu-O [17] lead to $t \approx 0.5$ eV. A reasonable value for U is 5 eV. For these compounds the difference in their T_c 's can be explained within the framework of this model by a difference in δ only. We assume that this also applies to Bi-Ca-Sr-Cu-O.

In the remaining part of this paper we will use the following expression for the function $f(t/U, \delta)$ proposed by Cyrot [18–20]:

$$f\left(\frac{t}{U}, \delta\right) = \frac{U\delta}{t} \exp\left(-\frac{U\delta}{t}\right). \quad (4)$$

Substituting this function into eq. (3) we obtain an expression for T_c . This function has been plotted in fig. 5a for the previous mentioned values $t=0.5$ eV and $U=5$ eV. A maximum is observed for $\delta=t/U=0.1$.

Substitution of (4) into (3) gives for the volume dependence:

$$\frac{d \ln T_c}{d \ln V} = \frac{d \ln t}{d \ln V} \left(1 + \frac{U\delta}{t}\right) + \frac{d \ln \delta}{d \ln V} \left(1 - \frac{U\delta}{t}\right) - \frac{U\delta}{t} \frac{d \ln U}{d \ln V}. \quad (5)$$

Since U is essentially an intra-atomic parameter, we expect $d \ln U/d \ln V \approx 0$. Therefore we neglect the last term of eq. (5). From numerous bandstructure calculations as well as from experimental work on the pressure dependence of the electronic structure of metals [21] one knows that $t \propto V^{-n}$ with $0.6 \approx n \approx 2.5$. For an estimate of $d \ln t/d \ln V$ we use $d \ln t/d \ln V = -2$ in eq. (5). The contribution of the first term of eq. (5) to $d \ln T_c/d \ln V$ is indicated by the dashed line in fig. 5b. If we further assume

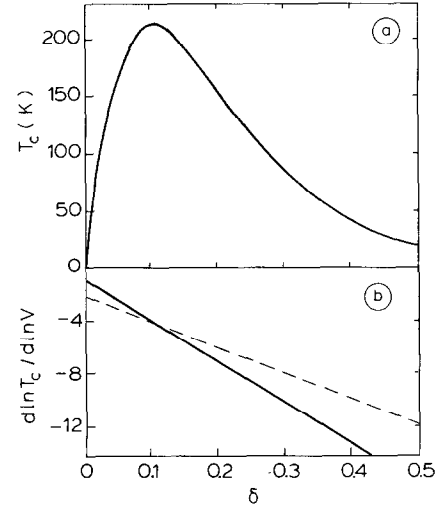


Fig. 5. (a) Dependence of T_c on the fraction δ of holes according to eq. (5) with $t=0.5$ eV and $U=5$ eV. (b) Volume dependence $d \ln T_c/d \ln V$ obtained from eq. (5) with $t=0.5$ eV, $U=5$ eV, $d \ln t/d \ln V = -2$ and $d \ln U/d \ln V = 0$ and (i) $d \ln \delta/d \ln V = 0$ (dashed line) and (ii) $d \ln \delta/d \ln V = 1$ (solid line).

$d \ln \delta/d \ln V = 1$ we obtain for the first two terms of eq. (5) the solid line of fig. 5b. If we combine eqs. (3)–(5) we are able to predict the correspondence between T_c and $d \ln T_c/d \ln V$. To compare this directly with experiment, this curve has been plotted in fig. 4. Although the agreement is at most semi-quantitative the present model predicts correctly the trend observed so far in $d \ln T_c/d \ln V$. It is important to note in this context that a simple calculation of $d \ln T_c/d \ln V$ within the standard BCS theory (with an attractive electron–phonon interaction) would lead to the wrong behaviour as $d \ln T_c/d \ln V > 0$ for all high- T_c superconductors, with large positive values when $T_c \rightarrow 0$ (see ref. [13]). From these pressure measurements one can thus conclude that the observed behaviour cannot be explained by a straightforward application of the BCS theory. If the model presented above gives a correct description of the system, conclusions with respect to the number of holes in the various compounds can be made. In particular the Y-Ba-Cu-O and Bi-Ca-Sr-Cu-O systems are characterized by a very small number of holes $\delta \approx 0.02$, whereas the La-Ba-Cu-O and La-Sr-Cu-O systems have a larger number of holes $\delta \approx 0.5$.

6. Conclusion

We have measured the T_c of a polycrystalline sample of Bi-Ca-Sr-Cu-O up to 80 kbar. The T_c at zero pressure is 92.4 K. The pressure dependence is linear with $dT_c/dp = -0.16$ K/kbar. We have estimated the T_c and its pressure dependence from a Hubbard-like model proposed by Cyrot. This calculation gives better agreement with experimental data than a straightforward application of the BCS-theory with electron-phonon coupling.

Further work on the 110 K-phase of Bi-Ca-Sr-Cu-O is in progress.

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