Solid State Communications, Vol. 70, No. 3. pp. 321-323, 1989
Printed in Great Britain.
0038-1098/89$3.00+.00
Pergamon Press plc

PRESSURE DEPENDENCE OF SUPERCONDUCTIVITY IN SINGLE-CRYSTAL $Bi_2(Sr,Ca)_3Cu_2O_8$

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(received Oct. 17, 1988 by M. Cardona
in final form Feb. 9, 1989)

The pressure dependence of the superconducting transition temperature (T_c) of a single-crystal sample of $Bi_2(Sr,Ca)_3Cu_2O_8$ was measured up to 42 Kbar. T_c first increased slightly with pressure, reaching a maximum at around 10 Kbar, and then decreased with increasing pressure at a rate of about 0.05 K/Kbar. This non-linear pressure dependence of T_c is discussed within a two-dimensional BCS model, and within two of the resonating-valence-bond models of high-T_c superconductivity.

Recently there has been much interest in superconductors with superconducting transition temperatures (T_c) above 77K, but containing no rare earth elements. One such family of the high-T_c superconductors are the Bi-Sr-Ca-Cu-O compounds[1,2]. The pressure (P) dependence of T_c has always played an important role in the attempt to understand the physical mechanism of superconductivity in these materials and in the search for materials with even higher T_c's. For example, Chu et al.[3] found that the La-Ba-Cu-O compounds had unusually large and positive values of dT_c/dP. This finding led these authors to substitute La with atoms with smaller ionic radii, such as Y, leading to the discovery of the Y-Ba-Cu-O family of superconductors[4].

In multi-phase samples of Bi-Sr-Ca-Cu-O, Chu et al.[5] found that T_c's reached maxima at relatively low pressures of about 12 Kbar and decreased at higher pressures, for superconducting phases with T_c's between 81K and 114K. A decrease in T_c at pressures above 14 Kbar was also reported by Wijngaarden et al.[6] in a polycrystalline sample of Bi-Ca-Cu-O with a T_c of about 85K. Most of the experiments on the pressure dependence of T_c in the new superconductors have been performed on polycrystalline samples, and have shown a wide range of values of dT_c/dP[7]. The variability in the pressure measurements is probably due at least in part to the presence of grain boundaries, which can differ greatly from sample to sample, and whose effects would be most prominent in the low-pressure regime. In this paper we report a measurement of the pressure dependence of T_c in a single-crystal sample of $Bi_2(Sr,Ca)_3Cu_2O_8$. We find that T_c first increases slightly with pressure, reaching a maximum at around 10 Kbar, and then decreases gradually with pressure to at least 42 Kbar. Our results above 10 Kbar were reproducible with pressure cycling, implying that the sample was not permanently altered by the high pressure. These results show that T_c depends nonlinearly on the lattice constant in this superconductor.

The crystals of $Bi_2(Sr,Ca)_3Cu_2O_8$ were grown from a mixture of Bi_2O_3, CuO, $SrCO_3$ and $CaCO_3$, with molar percentages of respectively 22.4%, 32%, 26.9% and 18.7%. The powders were mixed in a ball mill with acetone, then placed in a gold crucible and heated at 920 C for 5 hours and cooled to 820 C at a rate of 3 C/hr in flowing oxygen. The result was a black, glassy mass that cleaved into micacious sheets, with resistively determined T_c's of approximately 80K. X-ray analysis showed that the c axis was perpendicular to the cleavage plane and had a spacing of 3.0 nm, in agreement with the $Bi_2(Sr,Ca)_3Cu_2O_8$ compound identified by Subramanian et al.[8].

The sample used in this study was a thin platelet cleaved from the bulk crystalline mass, with approximate dimensions of 200x100x10 μm^3. Ohmic contacts were prepared by painting silver paint contacts on the crystal and baking them at 750 C for 20 minutes in oxygen. High-pressure measurements were made in a diamond anvil cell using an Inconel gasket and $CaSO_4$ as the pressure medium. Thin copper wires were introduced into the cell using the technique described by Erskine et al.[9], and attached with silver paint to the contact pads in a two-probe configuration; the residual contact resistance in the superconducting state was about 10 ohms. The pressure was measured with the standard ruby fluorescence technique. Four ruby chips were placed around the sample, and the pressure inhomogeneity was measured to be less than 10%. The sample temperature was determined with a calibrated Si diode thermometer in thermal contact with one of the diamonds. To minimize thermal lag, the temperature was changed slowly enough so that the resistance versus temperature curves during the cooling and warming cycles were identical. The sample pressure was first increased to 42 Kbar and then decreased to 14

Kbar with reproducible results, in contrast to some earlier experiments with polycrystalline high-T_c superconductors that showed irreversible changes in resistance with pressure cycling[10]. The experiment was discontinued when the wires were cut by the diamonds on repressurization. When the cell was opened, the sample was intact and showed no visible signs of damage.

A typical resistance versus temperature curve for the sample is shown in figure 1. At each pressure we define T_{co}, T_{cm} and T_{cf} as the temperatures where the sample resistance has dropped respectively by 10%, 50% and 90% of the total resistance decrease of the superconducting transition. The variation of these temperatures with pressure is shown in figure 2. The horizontal error bars represent the variation in

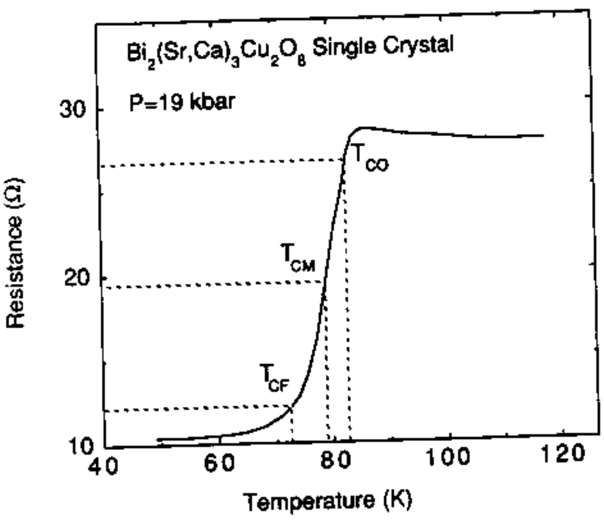

Figure 1. A typical resistance vs. Temperature curve showing the superconducting transition in $Bi_2(Sr,Ca)_3Cu_2O_8$ at high pressure.

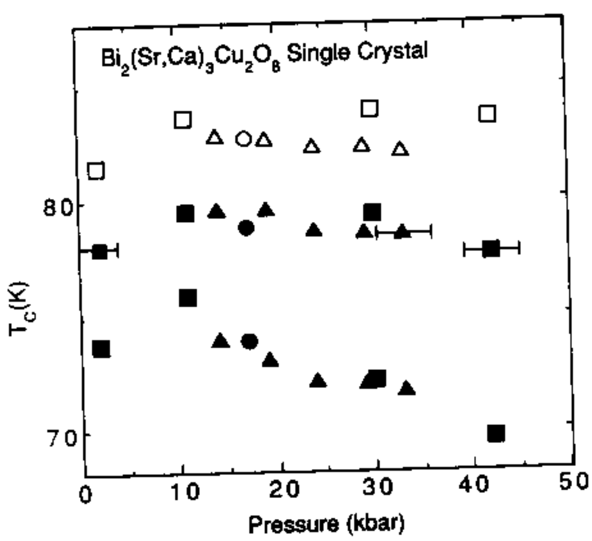

Figure 2. The pressure dependence of T_c in $Bi_2(Sr,Ca)_3Cu_2O_8$, showing T_{co} (open symbols), T_{cm} (dark shading), and T_{cf} (light shading). The differences in the symbols are explained in

pressure as determined from the ruby fluorescence measurements. The open squares are data points obtained with increasing pressure, and the triangles with decreasing pressure. The circle is the data point obtained on the second pressurization, before the wires broke. As can be seen in figure 2, the data for increasing and decreasing pressures are quite reproducible.

The results presented in figure 2 are in general agreement with previous results in polycrystalline samples of Bi-Sr-Ca-Cu-O. At pressures below about 10 Kbar, we find that T_{cm} increases at the rate of about 0.17 K/Kbar. Chu et al.[5] have reported an increase in T_c with pressure in Bi-Ca-Sr-Cu-O compounds at the rate of about 0.3 K/Kbar. Although this is a significantly larger rate, the uncertainty in both measurements could be substantial because T_c varies nonlinearly with pressure in this region. Above 10 Kbar, we find that T_{cm} changes at a rate of about -0.05 K/Kbar, with a pressure-induced broadening of the transition giving rates of -0.03 K/Kbar for T_{co} and -0.17 K/Kbar for T_{cf}. Winjgaarden et al.[6] report pressure dependences in T_{cm}, T_{co} and T_{cf} of respectively -0.16, -0.09 and -0.21 K/Kbar. The increased slope and additional broadening of their data is most likely due to the polycrystalline nature of their sample and to the higher pressures obtained (80 Kbar).

Recently, Griessen published a survey[7] of the pressure coefficients dT_c/dP in all of the high-T_c superconductors reported up to that time, and compared the data with predictions based on some of the proposed superconducting models. Only three of the models were considered to be consistent with the pressure measurements as well as with other experimental data: the two-dimensional BCS theory of Labbe and Bok[11], and the resonating-valence-bond (RVB) models of Cyrot[12] and of Fukuyama and Yosida[13]. Nonlinear dependences of T_c on pressure were not considered. Here we will discuss briefly how the nonlinearities observed in our data may be understood within these models.

Within the two-dimensional BCS model of Labbe and Bok[11], T_c is determined by the usual electron-phonon interaction parameter λ and by D, the "width" of the two-dimensional saddle point E_s in the electronic density-of-states, via the equation:

$$k_B T_c = 1.13\hbar D \exp(-1/\sqrt{\lambda}) \quad (1)$$

The expression for the volume (V) dependence of T_c is derived from Eq. (1) as

$$\frac{d(\ln T_c)}{d(\ln V)} = \frac{d(\ln D)}{d(\ln V)} + \frac{1}{2\sqrt{\lambda}}\frac{d(\ln \lambda)}{d(\ln V)} \quad (2)$$

To explain the saturation and nonlinear dependence of T_c on P, one or both terms in Eq. (2) has to be strongly dependent on V. Since there is no evidence of lattice instability or softening of the Cu-O vibrational mode involved in λ, there is no reason for it to have a strong nonlinear dependence on B. On the other hand, it is possible that D does have a strong nonlinear dependence on B. Labbe and Bok[11] assumed an exactly half-filled two-dimensional band so that the Fermi level coincided with E_s. This assumption would no longer be valid if pressure caused electrons in adjacent Cu-O planes to overlap, thus modifying the van Hove singularity and, in addition, shifting the Fermi level. In general, we expect that pressure will tend to cause any two-dimensional system to behave more like a three-dimensional system, so the singularity at the saddle point in any two-dimensional model should be very sensitive to pressure. In addition we note that the saturation and nonlinear dependence in T_c with pressure has been observed in conventional superconductors, such as La_3S_4 and La_3Se_4[14], where the data were interpreted as a pressure-induced shift of the Fermi level through a sharp peak in the density of states. Similar pressure-induced shifts of the Fermi level relative to the singularity may also contribute to the pressure effects in $Bi_2(Sr,Ca)_3Cu_2O_8$.

In the RVB models, T_c depends only on the transfer integral t_b and the electron-electron interaction U. It is not obvious why these quantities should possess strong nonlinear dependences on V. However, we note that the expression derived by Cyrot[12] for T_c depends on an additional parameter δ:

$$T_c = t_b \delta \exp[-U\delta/t_b] \quad (3)$$

where δ is the fractional doping which creates some Cu^{3+} ions. In this model T_c depends very strongly on δ, and in a very nonlinear way (see, for example, Fig. 3 of Ref. 7). Griessen assumed that only t_b depended on V, while U and δ were both independent of V. If δ is dependent on pressure, perhaps through a charge-transfer mechanism, it could account for the nonlinear behavior of dT_c/dP.

After this work was completed, we learned of a high-pressure study of single-crystal $YBa_2Cu_3O_{7-\delta}$ (ref. 15). Unlike $Bi_2(Sr,Ca)_3Cu_2O_8$, where the polycrystalline and single-crystal data are essentially in agreement, the single-crystal data in $YBa_2Cu_3O_{7-\delta}$ gives a value of dT_c/dP at high pressures that is opposite in sign to that of the polycrystalline data. At low pressures, the behavior of dT_c/dP is strongly dependent on the quality of the crystals. We attribute the variations in the $YBa_2Cu_3O_{7-\delta}$ data to the extreme sensitivity of this material to processing conditions and oxygen stoichiometry.

In summary, we find a nonlinear dependence of T_c on pressure in single-crystal $Bi_2(Sr,Ca)_3Cu_2O_8$, with a negative dT_c/dP at pressures above about 10 Kbar. We have shown how these results may be understood within a two-dimensional BCS model and within two of the RVB models of high-T_c superconductivity.

Acknowledgments - We thank Amy Liu for discussions, Paul Pinsukanjana for assistance with sample preparation, Mike Learner for the X-ray analysis, and Wei Shan for advice on preparing the diamond anvil cell. This work was supported in part by the Director, Office of Basic Energy Sciences, Material Science Division of the U. S. Department of Energy under Contract DE-AC03-76SF00098, and by a National Science Foundation Grant No. DMR-84-00041.

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