APPLICATION OF A DIAMOND ANVIL CELL FOR THE STUDY OF THE MAGNETIC SUSCEPTIBILITY OF CERAMIC SUPERCONDUCTORS UNDER HYDROSTATIC PRESSURE

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ABSTRACT

We report the development of a diamond anvil cell to study the ac susceptibility of ceramic superconductors to pressures above 10 GPa. Highly densified helium is used as pressure medium. The superconducting transition is detected inductively by a miniature coil system. Results on both $Y_1Ba_2Cu_3O_7$ and $Bi_2Ca_1Sr_2Cu_2O_{8+y}$ with different oxygen content y are presented and discussed within the context of pressure induced charge transfer.

I. INTRODUCTION

It is well known that high pressure experiments have played a major role in high temperature superconductivity since its discovery in 1986. One of the key pieces of information for better understanding these compounds is the dependence of their superconducting transition temperature T_c on pressure, as has been pointed out in several talks at this conference. By far the most data originate from experiments below 2 GPa, a pressure easily achieved by conventional techniques. However, since the compressibility of ceramic superconductors is not very large, most of these experiments are only able to detect a linear dependence between T_c and pressure. To learn more about the change of T_c with the lattice parameters, the pressure range should be increased considerably. This calls for the application of the diamond anvil cell (DAC). A number of groups have studied $T_c(P)$ [1,2] using the DAC technique, but generally under nonhydrostatic pressure conditions. Because of the inherent sealing problems, they use either (1) no pressure medium at all, (2) soft solids like NaCl or (3) fluids which lose their hydrostatic properties under pressure since they solidify. It remains an open question how meaningful such results are in the light of the strongly anisotropic dependence of T_c on lattice parameter anticipated for the layered structure of perovskite superconductors. In a recent paper, Meingast et al. [3] even find that the pressure dependence of T_c in $Y_1Ba_2Cu_3O_7$ has different signs along the a and b axes and is large in magnitude along these directions. They conclude that the small values so far reported from hydrostatic experiments on this system result from cancellation effects. Another system where hydrostatic or nonhydrostatic pressure experiments are known to yield differing signs and magnitudes of dT_c/dP is the La_3(chalcogenides) [4]. It is clear that more care should be taken in future high pressure studies of the oxide

superconductors to clearly define the effects of the pressure technique used.

Another important consideration for experiments applying the diamond anvil cell for the study of ceramic superconductors is that T_c normally is detected resistively. This might explain the inconsistent findings of different groups since a percolation path of superconducting material could be mistaken for bulk superconductivity.

Here we present a technique which overcomes the above shortcomings both by (1) using highly densified helium as the pressure medium and (2) detecting bulk superconductivity by an ac–susceptibility measurement. Also we measure on single crystalline material which excludes the granularity effects usually present in sinter samples. Since our experimental technique is rather uncommon, we first want to describe in detail the experiment, discussing the typical problems of such a measurement. Then we will illustrate the method by presenting $T_c(P)$–results on $Y_1Ba_2Cu_3O_7$ and recent measurements on $Bi_2Ca_1Sr_2Cu_2O_8$. On a given crystal we study how increasing the oxygen content effects the $T_c(P)$ dependence. Finally, we discuss these results within the recently proposed model of pressure–induced charge transfer.
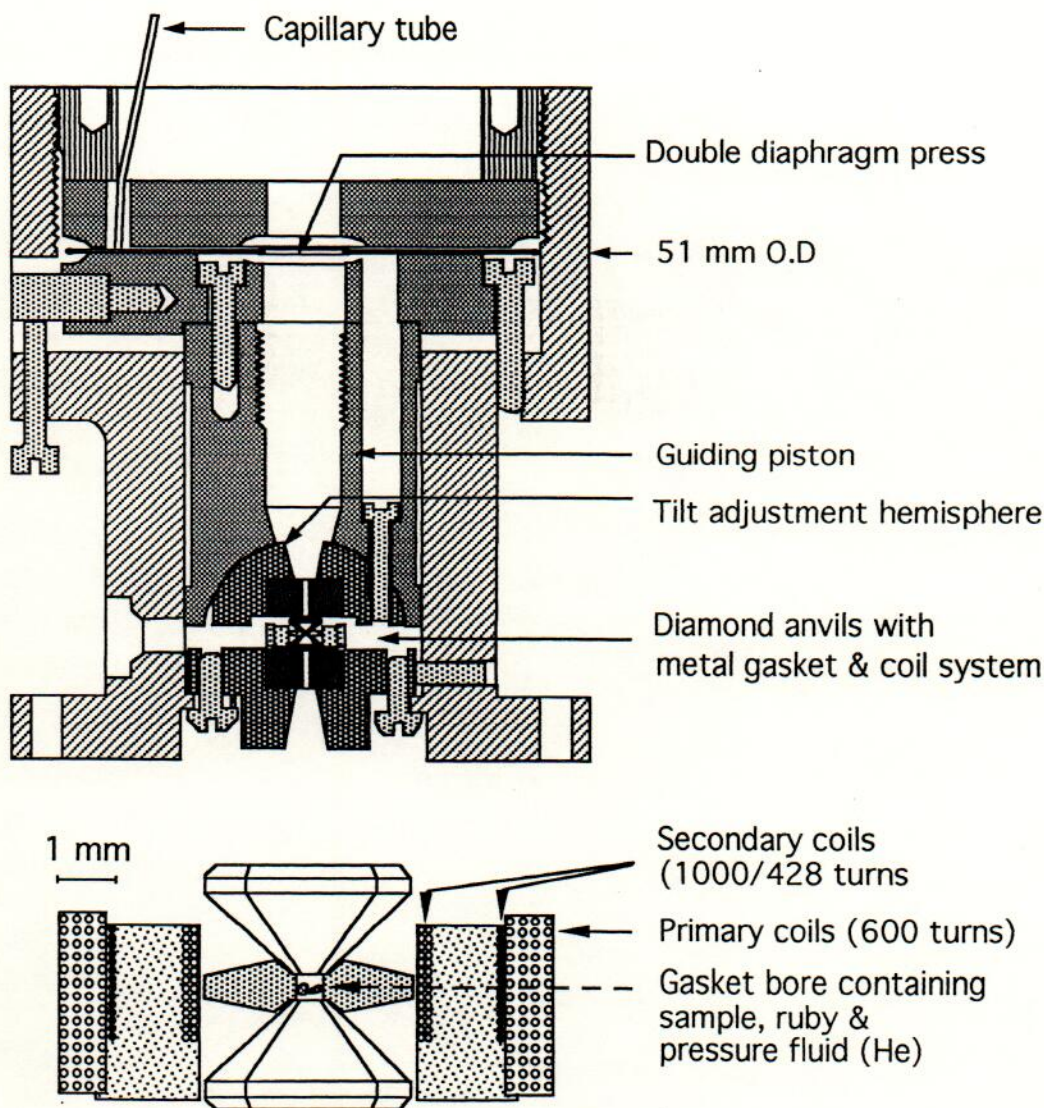

Fig. 1   Diamond–anvil pressure clamp for pressures above 10 GPa. Two 1/6 carat diamond anvils press into a 3 mm O.D. metal gasket with a 0.25 mm dia. bore containing sample, ruby manometer, and liquid He pressure fluid. An enlarged view of the primary(secondary) coil system using 30(16) μm dia. Cu–wire is also shown.

II. EXPERIMENTAL

Figure 1 shows our diamond anvil clamp [5] (DAC). It contains two 1/6 carat type I diamond anvils with 0.5 mm culet diameter mounted on B_4C plates. The rest of the clamp is made completely of copper–beryllium alloy, critical parts are made of magnetically pure binary CuBe. The force pushing the diamond anvils together is provided by a double diaphragm press [6] which can be pressurized to more than 200 bars of helium gas. The coil system used for the susceptibility measurement is placed around a 3 mm O.D. metal gasket as shown in the enlarged view. Primary (field) and secondary (pick–up) coils are made of 30 and 16 μm diameter copper wire, respectively, and are cast in epoxy. The two parts of the pick–up coils with 1000 and 428 windings are compensated to about 1% outside the clamp. Both carbon and platinum thermometers (not shown in Fig. 1) are placed inside the guiding piston, about 10 mm
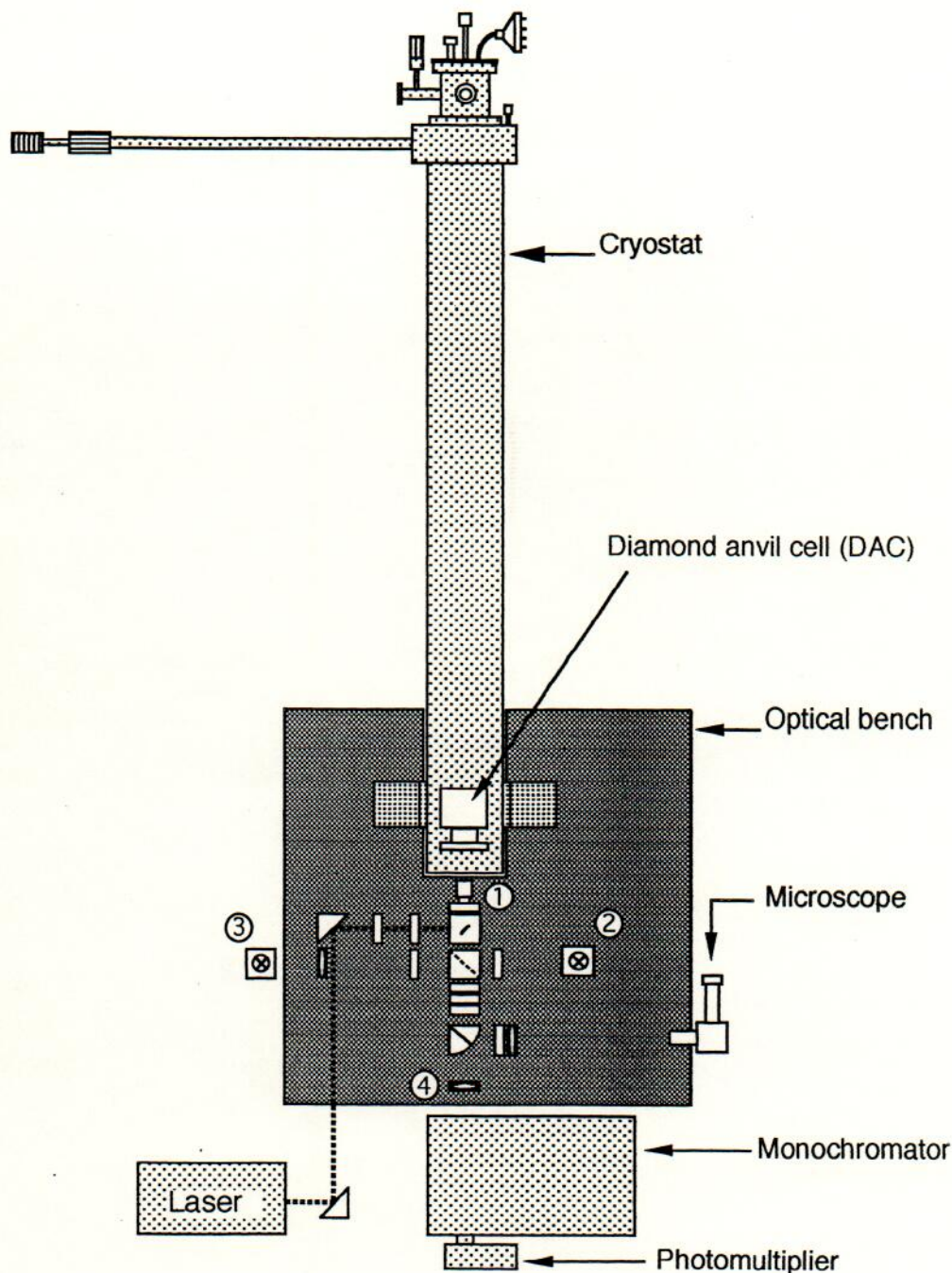
Fig. 2   Cryostat and optical set up for measurements using the diamond anvil cell (DAC). See text for details.

above the sample. A test measurement with four thermometers at different parts in the clamp showed temperature gradients to be less than 0.1 K in a typical measurement cycle between 50 and 150 K. The DAC is mounted on a holder and inserted into a continuous flow cryostat shown in Fig. 2. The top cover contains electrical feedthroughs (including four coax–lines down to the coils), a capillary connector and a feedthrough for a lightguide used to illuminate the cell from above. The cryostat has sapphire/quartz windows at the bottom. An optical set up below provides the possibility of both observing the cell and measuring the pressure via the standard ruby fluorescence technique [7]. The basic parts are: a collimator lens (1) (f = 88 mm) right in front of the window and focussed at the cell, a microscope consisting of an objective (1:10) and a ocular (5x), a white light lamp (2) for illumination of the cell, a neon lamp (3) providing reference lines, a lens (4) (f = 50 mm) focussing the fluorescence light onto the entrance slit (35 µm) of a 1/4 m monochromator and matched to its f/ number as well as some filters and polarizers. The ruby is excited by a 100 mW argon ion laser, but only 5 to 10 mW reaches the interior of the cryostat.

Helium as pressure medium

Helium is the best pressure medium known; it retains its hydrostatic properties in the solid state better than any other compound [8]. Its melting curve up to 300 K is fairly well given by Simon's equation [9]

$$P(GPa) = 0.0016067 \, T(K)^{1.565}$$

which means that it solidifies at room temperature only at about approximately 11.5 GPa. The equation of state (density vs. pressure) of helium is accurately known to 12 GPa from sound velocity measurements [10] as shown in Fig. 3. Unfortunately, it is difficult to load He into the cell at a high initial density. Two methods, high pressure loading at room temperature (typically at 0.1–0.5 GPa) and cryogenic filling near 4.2 K at ambient pressure have been reported so far [7,8]. In the present work we employ the latter technique and fill the cell according to the following procedure: first the cryostat is cooled to 4.2 K and liquid He filled in to cover the DAC. Next, by pumping on the He–bath the temperature of the DAC is lowered to 2 K so that superfluid He can enter the bore of the gasket. Finally, the cell is sealed off by pressing the diamonds together with a force of approximately 1500 N.
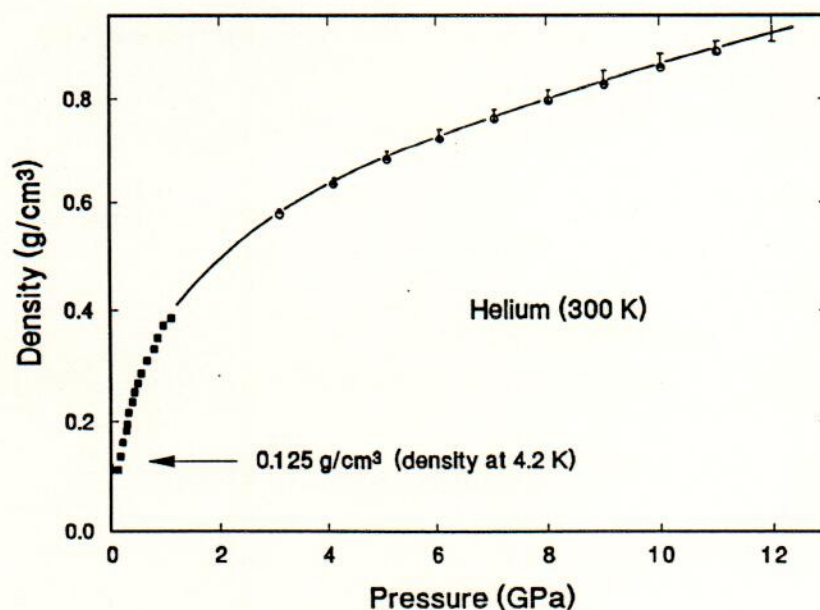

Fig. 3   Density of helium as a function of pressure at room temperature. Data was taken from Ref. 10. The density of the liquid is indicated for comparison.

From Fig. 3 we can deduce important information for the application of He as pressure medium. If liquid He is loaded into the cell at 4.2 K (density 0.125 g/cm), the volume of the cell has to be reduced by a factor of 3 to reach 1 GPa and by a factor of 7 to reach 10 GPa at 300 K. This requires a large bore diameter and a thick gasket at the start of the experiment. In our case we use a gasket with a 250 μm hole diameter and approximately 300 μm thickness preindented to 115–135 μm. Also, from the observed diameter of the cell and the data in Fig. 3 we are able to estimate the thickness of the gasket at a given pressure to help ensure that the diamonds don't squeeze directly onto the sample.

Gasket materials

The following requirements must be fulfilled for the gasket material used in an ac susceptibility measurement: (1) it must be nonmagnetic, (2) it should have a small electrical conductivity even at low temperature to minimize screening effects and, (3) it should possess a high tensile strength to allow measurements with relatively large samples. From the large number of gasket materials reported so far we carried out experiments with the following three: copper beryllium (10 at% beryllium, 0.3 at% Co) hardened for 2 h at 315 °C after preindentation, pure rhenium, and $Ta_{90}W_{10}$ [11]. All three are essentially nonmagnetic; Fig. 4a shows the measured electrical conductivity as a function of temperature. The tensile strengths at 300 K are 1.4 GPa, 2.2 GPa and 1 GPa for CuBe, Re, and $Ta_{90}W_{10}$, respectively [12]. Copper beryllium is the easiest to work with; however, in early experiments with a CuBe gasket and an ethanol–methanol pressure medium we did not reach pressures beyond 7–8 GPa. This might not only be due to the smaller tensile strength compared to Re, but also to the relatively large cell volume used in this experiment. In an attempt to reach higher
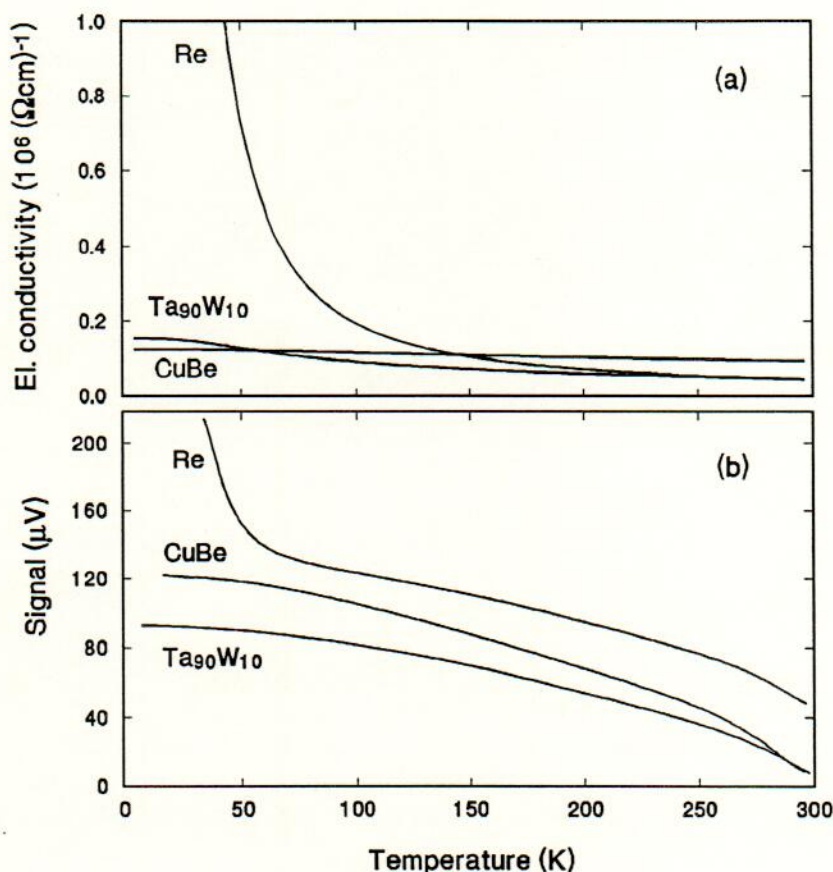

Fig. 4   Temperature dependence of (a) the electrical conductivity and (b) the background signal detected by the pick–up coils in measurements for three different gasket materials (Re, $Ta_{90}W_{10}$, CuBe).

pressures we tried gaskets made of pure rhenium 280 μm thick preindented to 100 μm. It takes considerably more effort to work with Re than with CuBe alloy. In particular, the bore can't be drilled in Re using standard techniques. We were successful in spark-cutting a 200 μm hole in the center of a 3 mm O.D gasket. Another disadvantage of pure rhenium is its relatively high electrical conductvity at low temperatures (Fig. 4a) which prevents measurements below 60 K due to a strong increase in the background signal (Fig. 4b) produced by eddy currents in the gasket. We finally tried a $Ta_{10}W_{90}$ alloy rolled to 290–330 μm thickness which proved to be the most suitable gasket material. This alloy is nonmagnetic, has a relatively small electrical conductivity at low temperature, and, despite its relatively low tensile strength, holds pressure very well due to the fact that it cold-welds to the diamonds. Fig. 5 shows a test measurement to 22 GPa with only helium and a ruby chip in the gasket bore. This measurement was interrupted to check the condition of the DAC; much higher pressures should be possible.
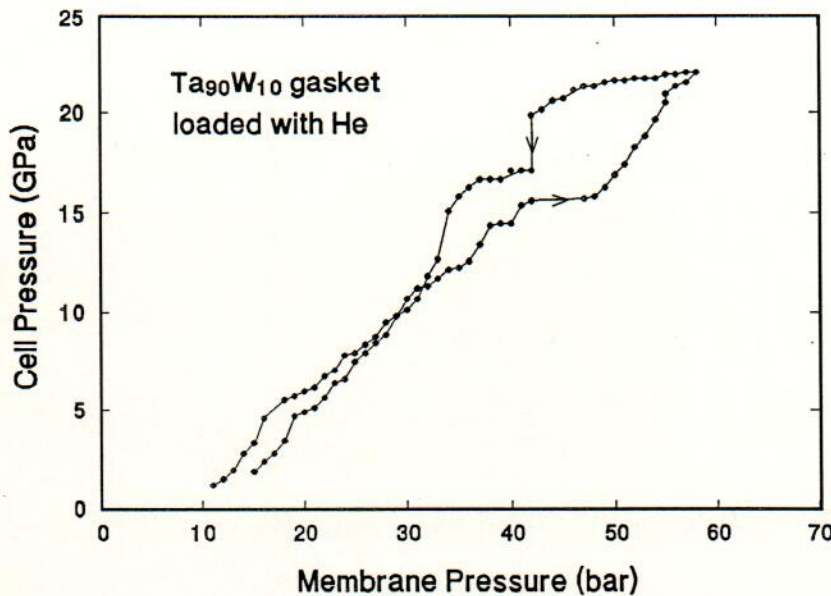

Fig. 5   Pressure in the cell versus pressure in the membrane (see Fig.1) in a test measurement using a $Ta_{90}W_{10}$ gasket loaded with helium. A pressure of 1 bar in the membrane creates a force of approximately 150 N on the diamonds.

T_c by an ac-Susceptibility Measurement

Using a compensated coil system like the one in Fig. 1, the signal from the transition of a perfect superconductor is expected to be given in SI units by [13]

$$U = \pi f B V \left[1/(1-D)\right] \left[N_i/R_i - N_o/R_o\right] \quad,$$

where f is the frequency of the applied ac-field B, V the sample volume, D the demagnetisation factor, and N_i/R_i and N_o/R_o the number of windings divided by the radius for the inner and outer pick-up coils respectively. For typical values (f = 500 Hz, B = 4 G, V = 1 x 10^{-4} mm³, D = 1/2, N_i = 1000, N_o = 428, R_i = 1.75 mm, R_o = 2.4 mm) we find U ≈ 50 nV. To recover such a small signal it is necessary to use a sensitive lock-in amplifier and avoid noise sources by proper shielding and grounding. Fig. 6 shows the circuit diagram of our measurement. The input of the lock-in amplifier (PAR 124) is connected to the pick-up coils via a variable inductance L. Due to the strong coupling of the metallic parts of the clamp and the gasket, the

pick–up coils are no longer compensated once the coil system is placed into the clamp. By adjusting the inductance L and the resistor R the resulting offset can be set to zero at any given temperature. The R–C–L unit constitutes a wide angle phase shifter. It has the advantage that both the phase (up to $\pm 90°$ relative to the ac field) and the magnitude of the signal can be varied independently, which is not possible in the classical Hartshorn bridge [14]. The choice of the right preamplifier is critical for noise reduction. Its noise characteristic must match the source impedance and frequency. We use a PAR 116 preamplifier operating in the transformer mode.
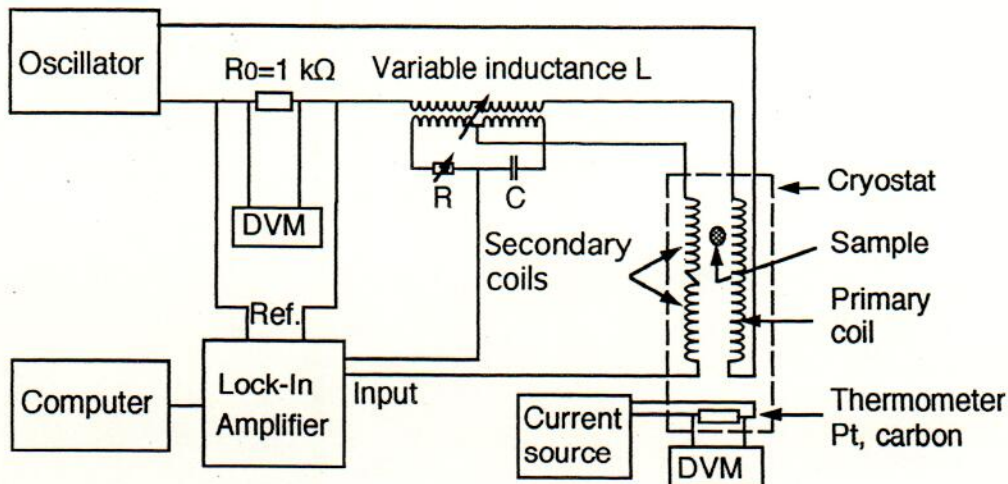

Fig. 6   Circuit diagram for ac susceptibility and temperature measurement systems. See text for details.
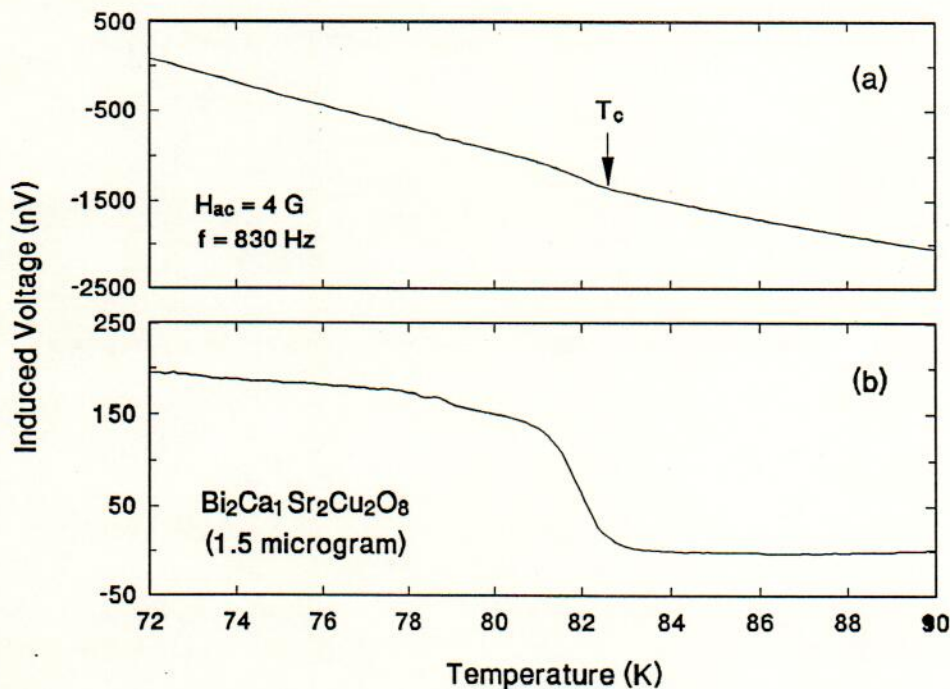

Fig. 7   Magnitude of χ_{ac} versus temperature for $Bi_2Ca_1Sr_2Cu_2O_8$ before (a) and after (b) subtraction of the temperature–dependent background.

In Fig. 7a we show the results of a measurement on a "fairly big" (1.5 μg heavy) single crystal of $Bi_2Ca_1Sr_2Cu_2O_8$ at 4.7 GPa pressure. As mentioned previously, the background signal is a sensitive function of the temperature. Part of this background is due to the proximity of the metallic pressure clamp and an imperfect compensation of the pick–up coils; however, the largest contribution comes from the gasket itself, especially below 60 K. As the temperature is lowered, the conductivity $\sigma(T)$ of the gasket (see Fig. 4a) increases and the penetration depth in SI units $\delta(T) = (1/\pi f \mu_0 \sigma(T))^{1/2}$ [15] of the ac–field at frequency f thus decreases ($\mu_0 = 4\pi$ 10^{-7} Vs/Am). Upon cooling, the gasket expels more and more of the applied ac–field which is detected by the pick–up coils leading to the slope in Fig. 7a. We conclude, therefore, that the temperature dependent background in Fig. 7a is the price which has to be paid in an ac–method whenever the field coils are placed outside the metal gasket as in the present case. After subtraction of the slope in Fig. 7a, the super–conducting transition becomes clearly visible, as seen in Fig. 7b.
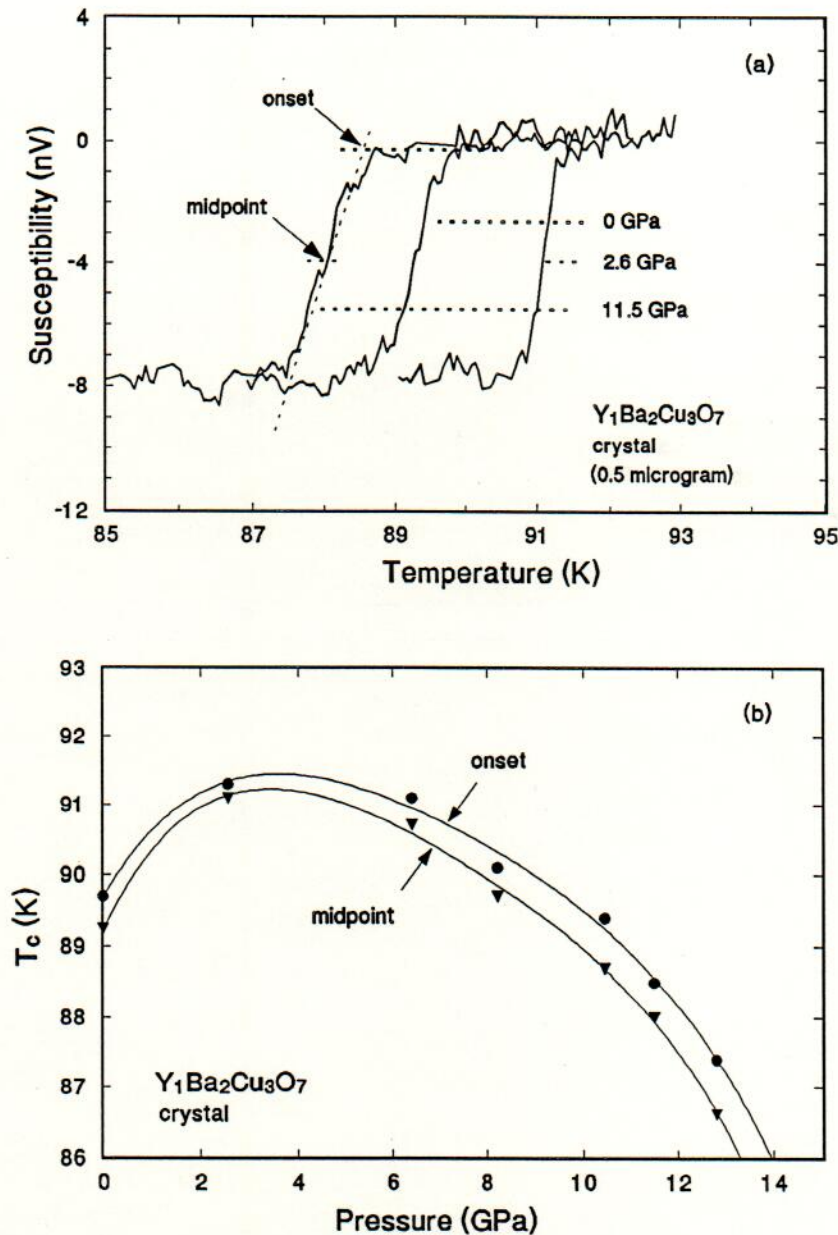

Fig.8 (a) Temperature dependence of ac susceptibility for a tiny crystal of $YBa_2Cu_3O_7$ at three pressures in the diamond–anvil clamp. (b) Superconducting transition temperature of a $YBa_2Cu_3O_7$ crystal versus pressure in the diamond–anvil clamp.

III. RESULTS AND DISCUSSION

One of the first measurements we carried out on high temperature superconductors was on a single crystalline sample of $Y_1Ba_2Cu_3O_7$, as seen in Fig. 8. Details of the experiment are published in Ref. 16. We find an initial increase of T_c with pressure at the rate (0.65 ± 0.15) K/GPa which agrees well with numerous "low pressure" experiments [17]. Among the few experiments reaching more than 10 GPa, there is poor agreement for the pressure dependence of T_c in the upper pressure range [17,18,19]. In our measurement we find that T_c reaches a maximum of 91.5 K at a pressure between 4 and 5 GPa. In an early experiment to 7 GPa using a 4:1 methanol-–ethanol mixture as pressure medium we find the same behavior.

What is the explanation for the maximum in T_c as a function of pressure? The essential problem in the interpretation of $T_c(P)$ data is that pressure simultaneously effects several parameters (orbital overlap, phonon frequency, carrier concentration, etc.) which may be crucial for high temperature superconductivity. One of the current beliefs is that the dominant effect responsible for the behavior of T_c under pressure is an increase of the charge carrier (hole) concentration in the CuO_2 planes. This has been derived from neutron scattering data by Jorgensen et al. [20] on $Y_1Ba_2Cu_3O_7$ to 0.6 GPa and by Wijngaarden et al. from recent measurements of H_{c2} and T_c as a function of pressure [21] for the 123 and Y–124 structures, even up to pressures above 10 GPa. A wide variety of experiments indicate that many, if not all, high–T_c superconductors lie on a general phase diagram which exhibits a bell–shaped maximum of $T_c(h)$ as a function of the hole concentration h. Assuming $Y_1Ba_2Cu_3O_7$ exibits such a phase diagram, a sample whose hole concentration is close to its optimal value would then be expected to show the following behavior upon pressure: increasing hole concentration would initially cause T_c to rise until its maximum value (corresponding to the optimal hole concentration) is reached; a further increase of the hole concentration with pressure beyond this point should lead to a decrease of T_c. This behavior is, in fact, observed in Fig. 8. Thus, our measurement would appear to support the idea of a pressure induced charge transfer.
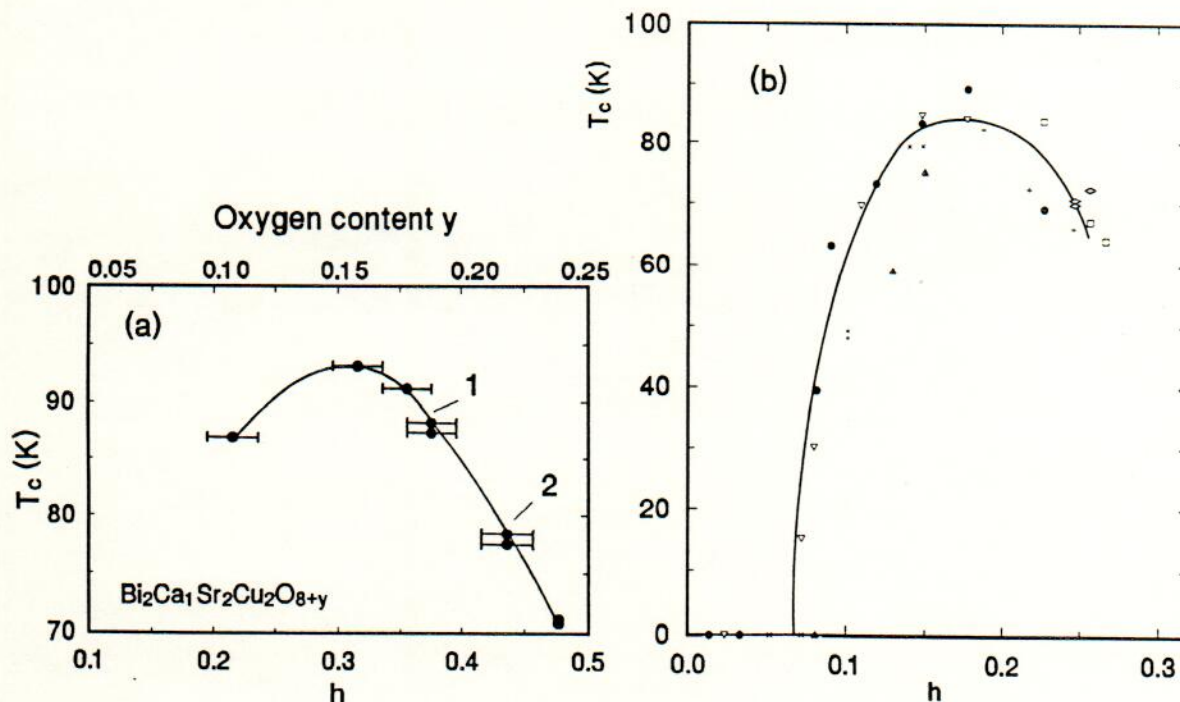

Fig. 9   Superconducting transition temperature T_c of $Bi_2Ca_1Sr_2Cu_2O_{8+y}$ as a function of the hole concentration h according to measurements by (a) Allgeier et al. [22] and (b) Groen et al. [23]. Numbers (1) and (2) refer to sample 1 and sample 2 of the present experiment.

To pursue this idea further, we carried out high pressure experiments on a different system, $Bi_2Ca_1Sr_2Cu_2O_8$. $Y_1Ba_2Cu_3O_7$ is not the ideal system since it shows only the left half of the above $T_c(h)$ phase diagram and the interpretation of data is complicated by the existence of the CuO chains which are a peculiar feature of the 123–structure. The system $Bi_2Ca_1Sr_2Cu_2O_{8+y}$ has two CuO_2 planes, no CuO chains and double BiO layers. As in $Y_1Ba_2Cu_3O_7$, the superconducting transition temperature T_c can be varied over a wide range by changing the oxygen content y. The additional oxygen, interstitially incorporated into the BiO layers, creates holes in the CuO_2 planes and renders the system superconducting. Figure 9 shows a measurement by Allgeier et al. [22] of T_c as a function of the hole concentration h. It is assumed that each oxygen atom creates two holes. In measurements by Groen et al [23] (Fig. 9b) the hole concentration was controlled by substitution of divalent Ca by trivalent Y (hole filling). Note the steep decrease of T_c in the latter experiments. Thus, for $Bi_2Ca_1Sr_2Cu_2O_8$, it seems to be clear T_c exhibits a well pronounced maximum as a function of the hole concentration.

Figure 10 shows the results of our pressure experiments on two samples of $Bi_2Ca_1Sr_2Cu_2O_8$ with different oxygen content. Both samples come from the same single crystal of excellent quality. It was grown from a stoichiometric mixture of the oxides, heated up to 980°C and then cooled down to 800°C at a rate of 1°C/h; this was followed by an anneal in O_2 to increase the oxygen content [24]. As confirmed by Raman scattering [25], the crystals were single phase and close to stoichiometric composition. Their orientation was determined using X–ray diffraction in trans-mission–Laue geometry. For the as–grown crystal, shielding and Meissner effect measurements with a SQUID magnetometer in a field of 12 mG parallel to the c–axis yielded a transition temperature $T_c \approx 86$ K, a transition width $\Delta T_c(10\%$ to $90\%)$ of 2.5 K, and a Meissner fraction of 42%. Sample 1 was broken off from the as–grown single crystal and measured in the DAC. After this experiment the original large single crystal was annealed for 12 h in flowing oxygen at 600 °C. A measurement in a different SQUID system at 1 G dc field showed a T_c of 80 K with transition width 4 K. Sample 2 was then cut off from this oxygenated single crystal for use in the pressure experiment. This measurement was carried out three times in all using different pieces of the oxygenated single crystal as indicated by different symbols in Figure 10.
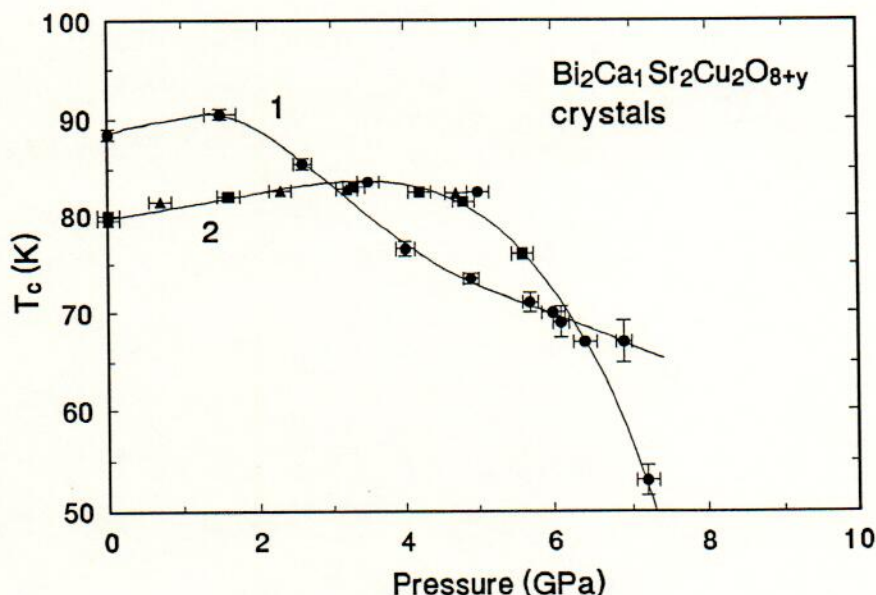

Fig. 10   Pressure dependence of T_c for samples 1 and 2 of $Bi_2Ca_1Sr_2Cu_2O_{8+y}$ for different values of the oxygen content y. The vertical error bars in sample 2 are approximately the same size as the symbols. See Fig. 9 and text for details.

In both samples we observe (see Fig. 10) an initial increase of T_c at a rate $\approx$ +1–2 K/GPa followed by a rather steep decrease after passing through a maximum. These results for the oxygen–rich sample reconcile reports of both a positive pressure dependence to 1 GPa by Goldstein et al. [26] and a negative pressure dependence above 2 GPa by Wijngaarden et al. [27]. The initial increase of T_c is also consistent with earlier results on polycrystalline $Bi_2Ca_1Sr_2Cu_2O_8$ samples with $T_c = 90$ K and 70 K of Sieburger et al. [28] to 0.6 GPa ($dT_c/dP = +1.5$ K/GPa) and a measurement by Diederichs on the latter ($T_c = 70$ K) oxygen–rich sample [29] to 3.2 GPa (+1.2 K/GPa). A positive pressure dependence is also reported by Forro et al. [30] to 2 GPa (+1.5 K/GPa), Kubiak et al. [31] to 1 GPa (+1.6 K/GPa), Beille et al. [32] to 1.5 GPa (+0.2 K/GPa), and Tamura et al. [33] to 1.5 GPa (+1.1 K/GPa) with critical temperatures at ambient pressure of 84 K, 82 K, 80 K and 88.5 K, respectively. No indications of the oxygen content relative to its optimal value were given.

The essential effect of oxygen loading is to shift the maximum from ≈ 1 GPa to ≈ 3.5 GPa. The overall increase of T_c with pressure is only 2–4 K, with the oxygen––rich sample being slightly larger. Comparing Figs. 9 and 10, it is tempting to conclude that the effect of pressure is to <u>fill</u> holes so that T_c passes through a maximum by going from right to left in the phase diagram of Fig. 9. This is exactly contrary to $Y_1Ba_2Cu_3O_7$ where pressure is believed to <u>create</u> holes in the CuO_2 planes. However, there are several shortcomings to the picture that pressure fills holes in $Bi_2Ca_1Sr_2Cu_2O_8$. First, we would expect that the increase of T_c with pressure should be much larger in the oxygen–rich sample, i.e. T_c should increase from 80 K to 90 K before decreasing. In fact, we observe an increase of only about 3 K. Second, we would expect a negative pressure dependence for a sample on the left hand side of the phase diagram. In an earlier experiment on a low oxygen polycrystalline sample of $Bi_2Ca_1Sr_2Cu_2O_8$ from a different batch using a helium gas system to 0.6 GPa, Sieburger [28] found that $dT_c/dP = +1.4$ K/GPa. The simple charge transfer model thus does not appear to be adequate. It can be argued that varying the oxygen content has structural consequences such as oxygen reordering effects. The actual hole concentration in the CuO_2 planes may therefore be quite different to what one expects from simply counting the number of interstitial oxygen in the structure. An experiment on a Ca substituted $Bi_2Ca_{1-x}Y_xSr_2Cu_2O_8$ would help to clarify this question.

We conclude that the present pressure experiments on oxygen–rich $Bi_2Ca_1Sr_2Cu_2O_8$ samples suggest that pressure may fill holes in the CuO_2 planes, in contrast to $Y_1Ba_2Cu_3O_7$ where it creates holes. However, the effect of pressure is clearly more complicated, since the positive pressure dependence for oxygen poor samples is completely unexpected in a charge transfer picture. The different behavior compared to $Y_1Ba_2Cu_3O_7$ might be related to the BiO–layers containing the additional oxygen and acting as charge reservoirs. Band structure calculations [34, 35] show two BiO bands, one contacts the Fermi level E_f from above, the other dips below E_f, leading to the formation of electron pockets in the BiO subsystem. Since the two layers are only loosely bound together, pressure might considerably change these bands and consequently the degree of doping of the CuO_2 planes, as pointed out by Hybertsen and Mattheiss [35].

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