Nonlinear Response of Type II Superconductors: A New Method of Measuring the Pressure Dependence of the Transition Temperature, $T_c(P)$

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Abstract

A technique of measuring $T_c(P)$ in the diamond anvil cell by the third harmonic of the ac susceptibility (V_{3f}) is described. It requires no background subtraction and allows the use of gasket materials made from hardened steels. In addition, the observed peak structure in the V_{3f} vs. T data allows regions with different critical temperatures to be distinguished. Results for single crystals (with typical size, 0.25 mm x 0.25 mm x 0.1 mm) of the $Tl_2Ba_2CuO_{6+\delta}$ and $YBa_2Cu_3O_{7-\delta}$ systems are presented. The effects of sample inhomogeneities and nonhydrostatic conditions are discussed.

1. Introduction

Conventional measurements have utilized ac susceptibility to determine the pressure dependence of the superconducting transition temperature, $T_c(P)$. Most groups use a primary coil coupled to two secondary coils: one containing the superconducting sample and the other empty for background subtraction [1,2]. Usually non-magnetic gasket materials with relatively large samples are used in order to separate the signal of the superconducting sample from the large, temperature dependent background of the gasket and the cell. This precludes reaching the highest possible pressures which are achieved by using high-strength gasket materials, such as Inconel and stainless steel, and small volumes of hydrostatic fluid. One group has solved this problem by measuring the second harmonic of the ac susceptibility [3]. Their technique relies on the use of a special non-magnetic stainless steel [4], which is not readily available and fairly complicated, custom-built electronics, required to reduce the size of the background signal.

We show in this paper that another approach, namely the measurement of the third harmonic of the ac susceptibility, can be used to determine $T_c(P)$ without the problems inherent in the above methods. Using readily available, off-the-shelf electronics and standard gasket materials (both magnetic and non-magnetic), one can build a simple system to accurately measure $T_c(P)$ of small samples. Such a measurement sees only nonlinear effects, such as the onset of flux motion in a superconducting sample and is not sensitive to the eddy currents produced in the gasket. Furthermore, our measurements show that even magnetic gasket materials do not contribute to the

background of the third harmonic signal. This technique can also be used to detect variations in T_C that can arise from inhomogeneous samples or from possible pressure gradients in the medium.

The basic principle of the measurement is that the third harmonic of the ac susceptibility gives a measure of the losses induced by flux motion in a type-II superconductor. Above T_C, the nonlinear effects are vanishingly small. Well below T_C, the critical current (j_C) is greater than the induced ac current in the sample. In this regime, the dissipation is small and the third harmonic signal is again too small to detect. Close to T_C, however, j_C drops to zero and hysteresis occurs in the presence of an alternating magnetic field. The surface loss, W, due to hysteresis, generates a signal (V_{3f}), at three times the fundamental frequency. Assuming a field independent critical current, Bean [5] found the surface loss induced by traversing the hysteresis loop to be:

$$W = \frac{H_0^3}{12\pi^2 j_c} ergs/cm^2 \quad ,$$

where H_o is the amplitude of the applied field. Because j_C goes to zero at T_C, a large peak is produced in sweeps of V_{3f} vs. T, giving an extremely sensitive means of detecting the transition. The shape and temperature dependence of the peak is strongly influenced by pinning. If there is no dc field applied, the sharp onset of V_{3f} coincides with T_C and the irreversibility temperature, T_{irr}. In the presence of larger dc fields, however, this onset occurs at a lower temperatures and only corresponds to T_{irr}. Unlike other proposed techniques for measuring T_{irr} , the V_{3f} peak is independent of sample dimensions and thus represents the true onset of irreversibility [6]. As a result, the third harmonic of the ac susceptibility has been studied and used extensively for characterizing type-II superconductors [7,8,9,10].

2. Experiment

The diamond-anvil-cell setup is shown schematically in Figure 1a. The bottom diamond is stationary; the top is moveable. Pressure is applied at room temperature by a screw which advances the upper diamond toward the lower one. The diamond culets are about 1 mm in diameter. Primary and secondary coils with 400 and 350 turns

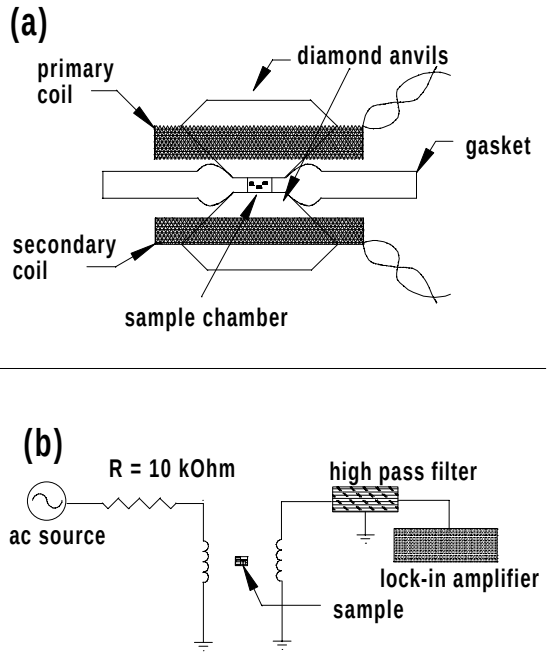

Figure 1. (a) The diamond anvil cell with primary (400 turns) and secondary coils (350 turns) (b) the circuit for measurement of the superconducting transition.

respectively are wound from 25 μm diameter wire and varnished onto the diamonds. The secondary coil is not counter wound, and neither is there a need for a bucking coil as in many experimental configurations. Unless

otherwise noted, the gaskets used in this study are made from hardened stainless steel, with thickness, 0.51 mm. The gaskets are pre-indented and a 0.48 mm diameter hole is drilled in the center.

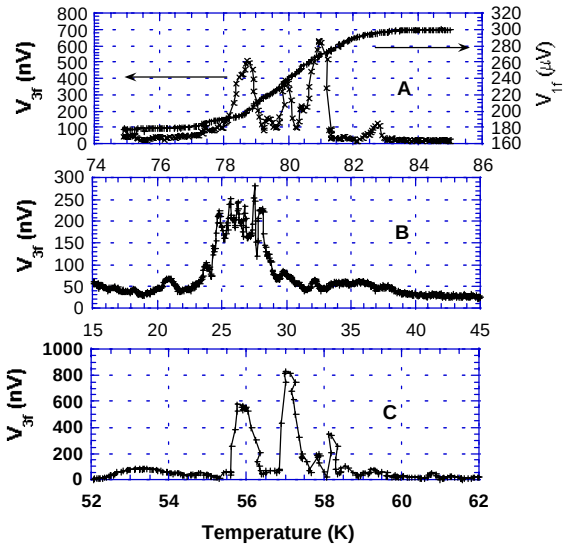

Figure 2. V_{3f} measurements on 1x1x0.1 mm Tl2201 single crystals. These crystals are five times larger than those used in the diamond-anvil cell and the panels illustrate the additional information gained by the third harmonic technique. (a) Comparison of the first and third harmonic techniques for the same crystal (b) V_{3f} vs. T for a Tl2201 crystal before annealing and (c) after annealing.

To prepare the cell, the gasket hole is loaded with small pieces of the superconductor and ruby chips for *in-situ* pressure measurements. Care is taken to leave ample room for the pressure medium (to prevent the diamonds from pressing directly against the sample) and to ensure a hydrostatic pressure before the medium freezes. As shown by Noack and Holzapfel, the shift in the R1 and R2 fluorescence peaks of ruby, $d\lambda/dP$, is thermally invariant [11]. The value of 0.365 nm/GPa is used to determine the pressure [12]. By measuring the difference between fluorescence produced by rubies inside and outside of the gasket, the pressure can be determined within an uncertainty of ±0.1 GPa throughout the temperature range of our measurements. The pressure medium used is silicon oil or an alcohol mixture, and the highest pressure achieved is 8.4 GPa. More specific details on the application and measurement of pressure in this particular cell are given elsewhere [1].

Figure 1b is a schematic of the circuit for measuring the superconducting transition. A lock-in amplifier [13] provides ac current to the primary coil. A five pole, passive, high-pass filter at the input of the lock-in is used to reduce the size of the fundamental voltage relative to that of the third harmonic [14]. In our experiments only the amplitude of the third harmonic signal is recorded. The fundamental frequency used is 10 kHz and the rms current supplied to the primary coil is 0.5 mA. With this current, the ac field from the coil at the sample is approximately 0.1 Oe.

3. Results and Discussion

A. Studies of $Tl_2Ba_2CuO_{6+\delta}$ at 0.1 Pa

Initial studies of inhomogeneities in superconductors and the effect of gasket materials on the third harmonic signal were carried out in a mock-up of the diamond-anvil cell. Figure 2a shows the superconducting transition for a single crystal of $Tl_2Ba_2CuO_{6+\delta}$ (Tl2201). For this measurement, the metal gasket was removed in order to make the V_{1f} signal observable in the raw data. The V_{3f} data show several peaks, each presumed to correspond to a different inhomogeneous region within the sample. In the first harmonic voltage (Fig. 2a), these inhomogeneities produce a broadened transition. Figure 2b shows a different Tl2201 crystal with a broad transition centered at 27 K. Figure 2c shows the transition for the same sample after

annealing at 400 ^{o}C for 16 hours in helium gas. The sharper transition at a higher T_C indicates that the sample is now reduced and more homogeneous with respect to oxygen content.

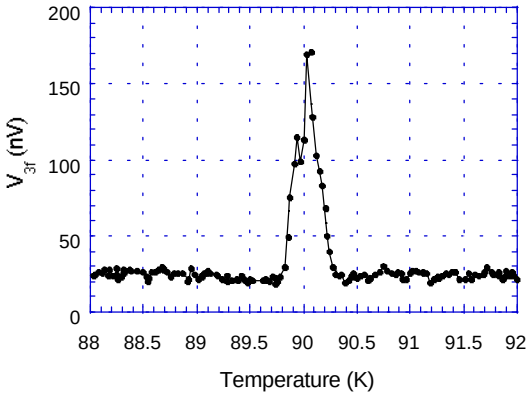

Figure 3. Transition of a YBCO single crystal in the presence of a hardened Inconel gasket. There is no detectable signal from the gasket.

Figure 3 shows the transition of a $YBa_2Cu_3O_{7-\delta}$ (YBCO) sample placed in the gasket hole of a 0.28 mm thick hardened Inconel gasket. Even though the gasket is magnetic, it produces no measurable effect on the background or the noise level of the signal. In conventional ac susceptibility, the signal from the magnetic gasket would dominate and the superconducting transition would be difficult to observe.

B. Studies of YBCO Under Pressure

T_C(P) for YBCO was measured with silicon oil and with a methanol/ethanol mixture as the pressure medium. A comparison of these studies shows that, unlike conventional ac susceptibility measurements, the third harmonic technique can be used to detect structure within the transition due to non-hydrostatic conditions.

T_C(P) data for YBCO with silicon oil as the pressure medium are shown in Figure 4.

After each run, the diamond anvil cell is warmed to room temperature for 16 hours,

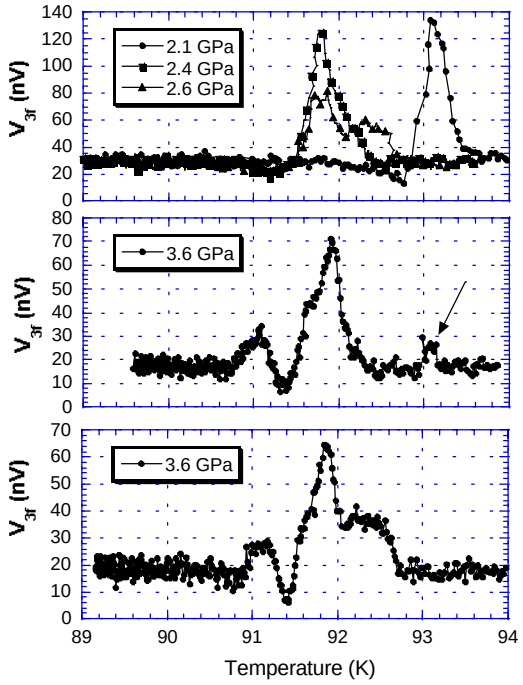

Figure 4. T_C(P) measurements on YBCO. The 3.6 GPa show 3 distinct peaks. Small changes in the peak structure are seen after warming the cell to room temperature for 16 hours.

the pressure is increased, and the cell is cooled again. At 0.1 Pa the sample displays a transition at 89.7 ± 0.3 K, where T_C is defined by the center position of the peak. The transition remains relatively sharp at 2.1 GPa and T_C increases to 93.1 K. The increase in T_C is consistent with an earlier T_C(P) study on a YBCO sample with a similar 0.1 Pa transition temperature [15]. At 2.4 GPa, T_C(P) decreases to 91.8 K, while the base of the peak broadens. At 2.6 GPa the peak broadens further, while separating into two distinct regions. When the pressure is increased to 3.6 GPa, peaks appear at 91.1 K , 91.9 K and 93.1 K. Finally, the test at 3.6 GPa was redone after warming the cell to room temperature for 16 hours. As seen in

Fig. 4, the 93.1 K peak has disappeared and a shoulder appears between 92.0 to 92.8 K.

The broadening of the superconducting transition in $T_C(P)$ tests has been observed in other measurements, such as resistivity and the first harmonic of the ac susceptibility [1,16]. However, such techniques usually define T_C to be the onset or midpoint of the transition and the problem of the width is ignored. The above results show that such a definition of T_C may not accurately represent what is really a set of distinct critical-temperature regions within the sample [17].

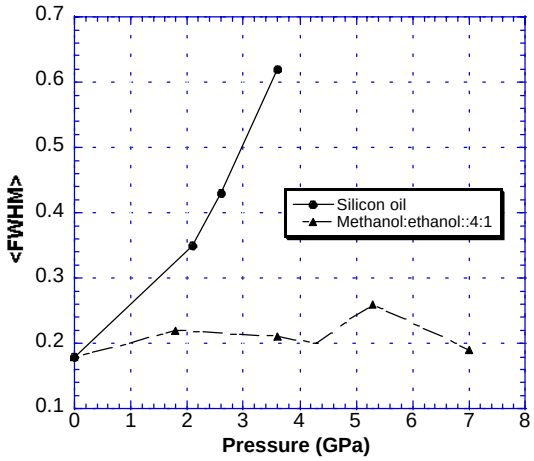

Figure 5. The full width at half maximum (FWHM) average of the two ruby fluorescence peaks vs. pressure for a silicon oil medium and a methanol:ethanol::4:1 mixture. The data are the resulting spectra from three ruby chips distributed throughout the pressure medium and are measured at T = 92 K.

The pressure medium used in the above experiments was silicon oil, which proved to be non-hydrostatic above 2 Gpa, at T = 92 K, as indicated by a broadening of the two ruby fluorescence peaks. Figure 5 shows a comparison of the homogeneity of the silicon oil and a 4:1 methanol/ethanol mixture by plotting the full width at half maximum (FWHM) average of the two fluorescence peaks versus pressure. The data acquired in the 4:1 alcohol mixture show little or no broadening up to 7.0 GPa, whereas data measured in silicon oil show significant broadening over this range. This is convincing evidence that silicon oil should not be used to obtain high pressures at low temperatures, and that the appearance of structure in the $T_C(P)$ measurements with the silicon oil may be due to an inhomogeneous pressure environment.

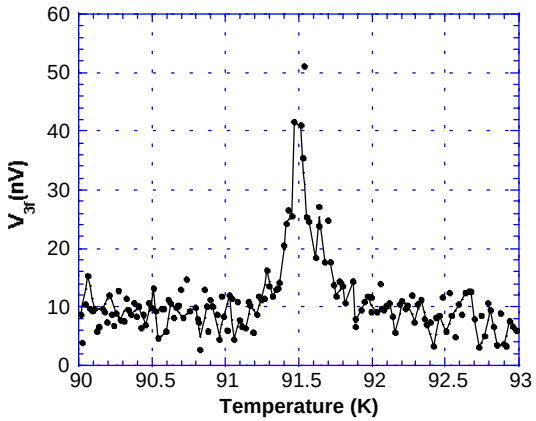

Figure 6. V_{3f} of the second YBCO sample at 0.1 Pa and with no dc magnetic field.

To further study the pressure-induced broadening of the superconducting transition, $T_C(P)$ measurements were made on a different sample of YBCO with a methanol:ethanol::4:1 mixture as the pressure medium. At 0.1 Pa, the data show a peak at 91.5 K with 0.2 K FWHM (Figure 6). At 1.7 GPa, with a 10 Oe dc field applied, the peak broadens and becomes asymmetric (Figure 7). This asymmetric shape is characteristic of type-II superconductors in the mixed state [6,7].

Similar to results obtained with the silicon oil medium, the application of higher pressures results in additional peaks within the transition. Figure 8 shows typical results at 4.2 GPa. The left and the right most peak are both distinguishable at pressures between 1.8 to 7.0 GPa.

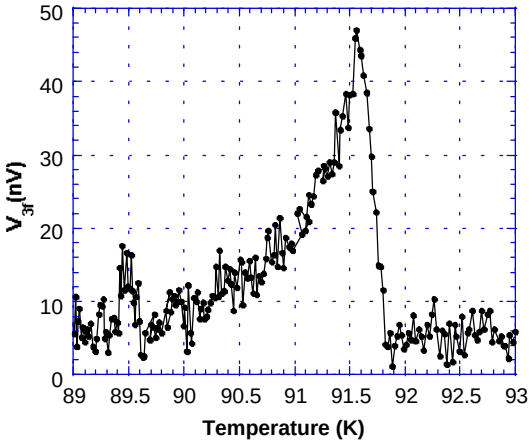

Figure 7. V_{3f} of YBCO sample at 1.7 GPa with a 10 Oe dc field.

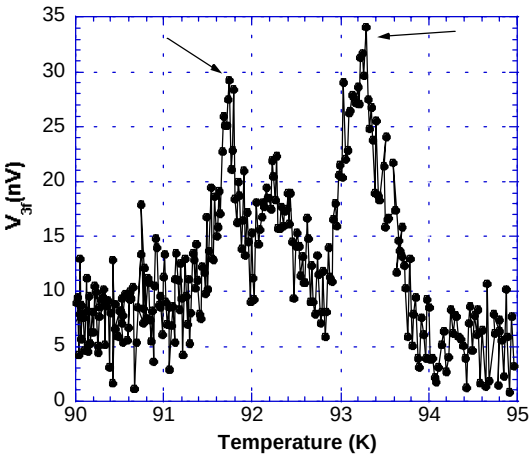

Figure 8. V_{3f} of YBCO sample at 4.2 GPa. Arrows indicate the left and right most peaks which can be followed from 1.8 to 7.0 GPa.

Figure 9 shows $T_C(P)$ for the two peaks with no field and with a 10 Oe dc field applied. The error bars in the graphs represent the estimated FWHM of the peaks. The data for the two peaks are similar in that the FWHM for both do not change measurably with pressure. A conventional measurement of V_{1f} would show a transition progressively broadened from 0.2 K to 2.3 K, as the pressure increased from 0.1 Pa to 7.0 GPa.

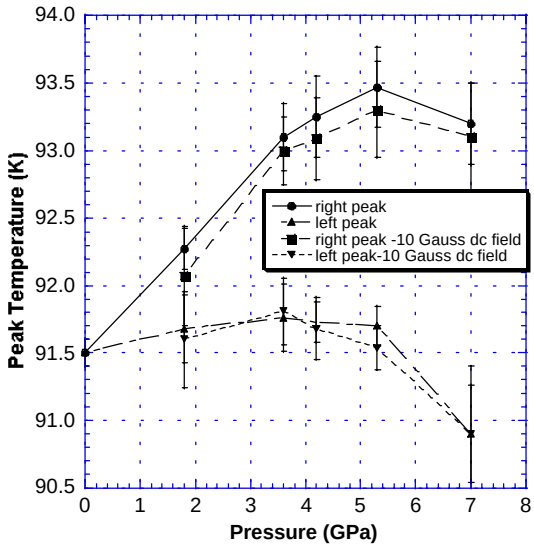

Figure 9. The position of the left and the right most peaks as a function of pressure for the YBCO sample. The error bars are an estimate of the FWHM of the peaks. Results with and without a 10 Oe dc field are shown.

The pressure dependence of the two peaks is strikingly different: the right peak is especially sensitive to the lower pressures, while the position of the left peak remains virtually unchanged. The measurements made in the 10 Oe dc field follow those without the field except for a slight offset. There are several possible explanations for this, however, the FWHM data in Figure 5, measured at T = 92 K, indicate that the pressure is hydrostatic. One possible explanation is that the application of pressure induces an inhomogeneous reordering of oxygen in the sample, similar to results obtained in the Tl2201 system.[18] A more likely explanation stems from the intrinsic oxygen inhomogeneity of these samples. For inhomogeneous samples, with domains of optimally- and under- doped material, the regions could have nearly the

same T_c, but very different $dT_C(P)/dP$ ratios.[19] X-ray studies will be performed to resolve this issue. Similarly, the inhomogeneities could be manifest as inter- and intra-granular effects which are exaggerated by the application of pressure. Studies of this effect in high magnetic fields are underway to clarify this.

Acknowledgments

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