2

AD-A264 340

:UMENTATION PAGE

Form Approved
OMB No. 0704-0188

...den is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this ...including this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson ...and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

2. REPORT DATE

3. REPORT TYPE AND DATES COVERED
Annual & Final Report 8/1/90 - 1/31/93

4. TITLE AND SUBTITLE
Sensitive detection of new superconductors created at ultra high pressures

5. FUNDING NUMBERS
AFOSR-90-0365

6. AUTHOR(S)
Dr Sheldon Schultz

DTIC ELECTE MAY 1 7 1993 S C D

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Univ of California
9500 Gilman Drive
La Jolla, CA 92093-0934

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NE
110 Duncan Avenue Suite B115
Bolling AFB DC 20332-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
2306/C1

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

See Report for Abstract

93-10696

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18

First Year and Final Progress Report
AFOSR-90-0365
8/1/90 - 1/31/93 (including 2 no-cost extensions)
Sheldon Schultz, Principal Investigator
"Sensitive detection of new superconductors created at ultra high pressures"

This technical report covers the work performed over a one and one-half year period under AFOSR Grant number 90-0365. Section I-III constitute the First Year progress report, and Sections V and VI cover the remaining period including that of the no-cost extensions.

I. Technical Goals and Initial Proposed Program

In the original proposal we presented the evidence that by utilizing Low Field Modulated Microwave (LFMM) spectroscopy we could sensitively detect the onset of superconductivity in either films, pellets, or single crystals. The technique does not require leads, nor a percolation path, and is unperturbed by the presence of other non-superconducting phases. We suggested that by incorporating this technique in conjunction with the diamond anvil cell approach to high pressures, we could open up new opportunities for rapidly and sensitively studying the significant phase space corresponding to the pressure axis. The primary goal was to detect new normal metal to superconducting phase transitions, starting for example, with those copper compounds for which interesting transitory pressure effects had been reported many years prior to the discovery of the superconducting cuprates.

We proposed to build the apparatus in a manner that enabled us to also observe regular electron spin resonance (ESR) under ultra high pressure conditions. Thus, in addition to sensing the normal metal to superconducting transitions, we would be able to detect transitions to ferromagnetic, AF, insulator, and their inverses as well.

We proposed that we would approach the development of the technique during the specific contract period in two phases or pressure ranges.

(1) sapphire anvil configuration, pressures 0-50 kbar
(2). diamond anvil cell- pressures to 150 kbar

Our experiments and results in this program are discussed in what follows.

II. Sapphire anvil configuration

We chose to initially pursue the sapphire anvil configuration for many reasons: (i) we would not have to immediately incorporate diamonds, but could learn with a cheaper larger system with which we were already familiar; (ii) previous workers had reported that sapphire anvils could be used with ESR to an interesting pressure range (0-50 kbar); (iii) larger samples could be used; (iv) we could utilize the pressure shift of the *in situ* ESR in Cr^{+++} ions in a ruby chip as a pressure calibration, thereby avoiding the used of the optical technique normally needed.

Our early tests were based on a structure adapted to an ESR cavity design we had developed utilizing amorphous aluminum oxide. This represented a very simple approach, which we knew to be limited to modest pressures, under 15 kbar. A diagram of this configuration is shown in Fig. 1. In Fig. 2 we present our data obtained in this system for the shift in the zero-field splitting of the Cr^{+++} states as a function of pressure. An example of the ESR spectra is presented in the inset. These data are in satisfactory agreement with that previously reported in the literature.[1] Based on these initial results we continued development of a more sophisticated structure, as described in an article in the literature, that was presented as useful up

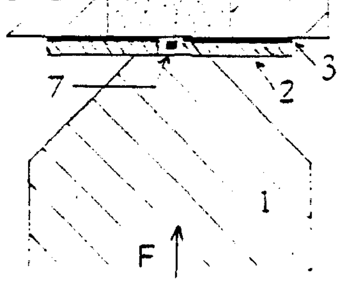


Figure 1. Initial moderate pressure ESR design . (1) Beryllium-copper anvil, (2) beryllium copper gasket, (3) indium metal seal, (4) microwave cavity block, (5) microwave port, (6) microwave cavity, (7) sample. The microwave cavity is filled with amorphous aluminum oxide. A force, F, applied to the anvil, pressurizes the sample which is placed in the gasket hole containing a Si grease medium.

to at least 50 kbar.[1] Unfortunately, we encountered complications. We subsequently found out from personal conversations with the authors of the paper we were relying upon, that the approach they reported was not reliable. In fact, the device was not really useful to 50 kbar because their sapphire cylinders were irreversibly damaged following every such run they had tried! At that point, despite the effort that we had already invested in developing the sapphire anvil system, we decided to forego further development and immediately switch to the diamond anvil cell approach.

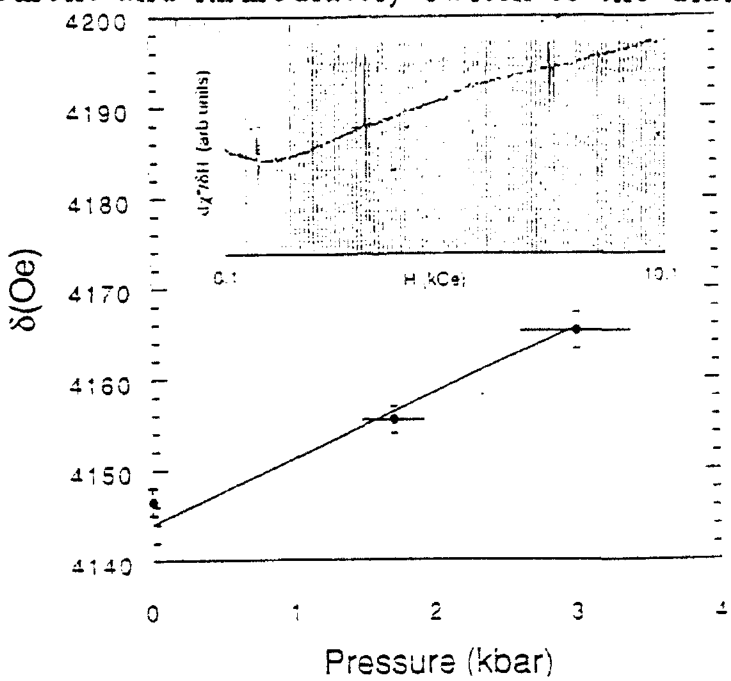


Figure 2. ESR data of the zero-field splitting, δ, of ruby as a function of pressure utilizing the configuration shown in Fig. 1. The solid line is the dependence as measured by Barnett, et al (Ref. 1). The inset shows the ESR spectrum of ruby for a magnetic field applied parallel to the c-axis. δ is determined from the field separation of the two resonances occurring at highest magnetic field.

III Diamond anvil cell development.

It should be appreciated that while it is now relatively easy to simply purchase a small diamond anvil cell, it is quite another matter to incorporate a suitable design for the LFMM technique. There are three main design problems: (i) the diamond anvils, backup pushers, etc. must all be placed inside a suitable microwave resonant structure; (ii) the allowable sample volumes are very small, and therefore the sensitivity of the microwave spectrometer must be optimized; and (iii) the metal gasket normally used in diamond anvil cells tends to shield the microwaves from reaching the sample. Suffice it to say that there are many possible approaches, some of which we tried, and found wanting. We also considered using non-metallic gaskets as developed by our colleague Professor Brian Maple. The primary limitation of this approach is that there is a low sensitivity due to the small ratio of sample to cavity volumes. Thus, we decided to pursue the dielectric loaded cavity design discussed in the following section.

IV. Final Diamond Anvil Cell Design

Near the end of the funding period we developed a design which essentially combined a microwave cavity with a Merrill-Bassett diamond anvil cell. One of the diamonds was designed to be an integral part of a dielectric TE101 cavity. In this scheme one actually needs the metal gasket of the pressure cell to serve as one of the cavity walls. This design is presented in Fig. 3. There is some loss of signal due to the shielding of the cavity microwave field from the sample inside the gasket hole, but tests with DPPH (a spin material) indicated that there was adequate sensitivity to warrant construction and testing. Unfortunately, we were not able to fully implement this design before the expiration of the grant funds. We remain convinced that we could complete our instrument with a modest amount of support, and hope to do so in the near future.

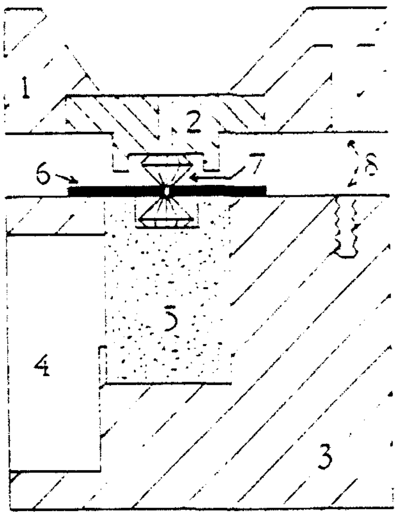


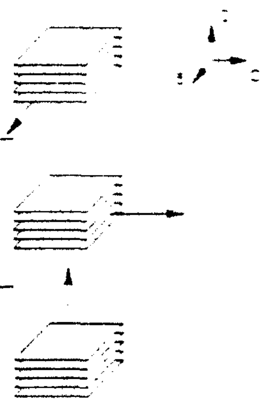
Figure 3. Final diamond anvil cell design. (1) Triangular platen, (2) diamond support disk, (3) microwave cavity block, (4) microwave port, (5) microwave cavity containing amorphous aluminum oxide and one diamond anvil, (6) 0.5 mm thick beryllium copper gasket with ~0.3 mm diameter hole containing sample(s) and pressure medium. (7) diamond anvil. The triangular platen and microwave cavity block have three symmetric locations, (8) for applying pressure with screws, three symmetric alignment pin positions (not shown), and three set screws (not shown) for positioning the upper diamond anvil.

V. ESR and superconducting sample sensitivity experiments.

The use of diamond anvils now entailed much smaller samples compared to those utilized in the amorphous aluminum oxide anvil tests. We therefore initiated a series of experiments to provide sensitivity calibrations for both the detection of the LFMM superconductivity signal, and the measurement of the internal pressure by the ESR zero-field splitting shift. We found that the signal amplitudes of both types of samples did not scale with volume as expected. Rather, as the sample volume was reduced the signals were significantly weaker than would be expected from scaling arguments. This reduction is really a coincidence, as the underlying mechanisms for the signals in each type of sample are quite different. We suspect that the ESR linewidth in the ruby chips may be broadened by strains and surface effects that become more pronounced for smaller samples, resulting in a weaker signal. We believe that this broadening of the ESR linewidth can be eliminated by proper annealing or sample preparation of the ruby chips.

On the other hand, the LFMM superconducting signature depends on the dissipation of flux near T_c, and we had no prior experiments or theory to guide us in explaining a size effect. In order to resolve these questions we started a series of tests which included the possibility that for very small samples we were likely seeing individual crystallites. We needed to clarify the dependence of the LFMM signal upon the relative orientations of the dc magnetic field, the microwave magnetic field, and the crystallographic axis. This required a cubic shaped Y(123) sample which we were able to obtain from Dr. F. Lucci in Italy. The results of these tests were rather surprising and are shown in Fig. 4. Note that for some relative orientations the effective signal can be reduced by more than an order of magnitude. In similar tests on thin Y(1:2:3) and NbN films we have found even larger reduction factors (up to 3 orders of magnitude) when the dc and microwave magnetic fields are not both oriented perpendicular to the film plane. In collaboration with Professor Herb Shore (SDSU) we have tried to understand these results in terms of the theory of Coffey and Clem.[2]. We have made progress in terms of understanding the generalized signal lineshapes as a function of temperature, but a full explanation of the orientation dependent amplitude is still not available. We are currently continuing these tests and theoretical modeling because they also bear directly on the use of the LFMM technique in the more macroscopic sized samples commonly used.

	a	b	c
a	37	45	12
b	42	32	4
c	144	122	72



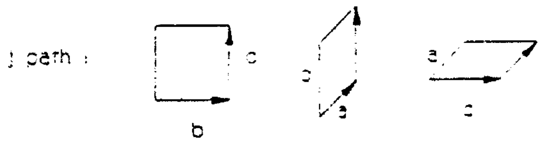


Figure 4. Low field modulated microwave (LFMM) absorption signal amplitude from a single crystal Y(1:2:3) cube for various orientations of the microwave magnetic field, h_{rf}, and the applied dc magnetic field, H_0, relative to the principal crystalline axes. The diagrams on the right hand side of the table indicate for each row the orientation of H_0 relative to the crystal planes. The diagrams at the bottom of the table indicate for each column the microwave current path direction induced by the field h_{rf}.

We have also spent considerable time improving the sensitivity of our microwave spectrometers. We have performed noise measurements on numerous GaAs FET microwave amplifiers from various manufacturers in conjunction with tests in homodyne and superheterodyne spectrometer configurations. We have found that a homodyne configuration utilizing a MITEQ 8-12 GHz, 26 dB gain amplifier can improve on the sensitivity of our current superheterodyne spectrometer by as much as a factor of 5 at high microwave powers (Fig. 5)! We have nearly completed construction of an improved version of this homodyne configuration which should greatly aid in the signal detection of the tiny samples that one must use in diamond anvil cells.

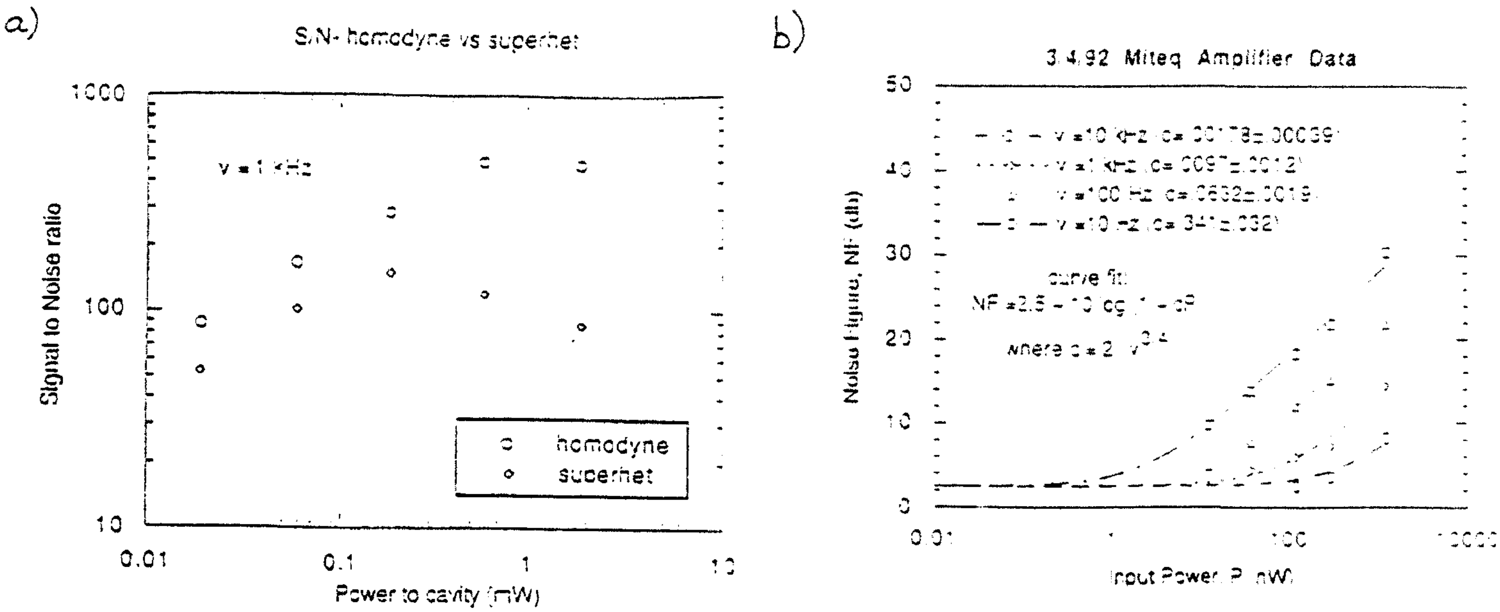


Figure 5 (a) Comparison of spectrometer sensitivities (expressed as signal-to-noise ratio (s/n)) as a function of microwave input power. ◇ - our current superheterodyne spectrometer, ○ - homodyne spectrometer utilizing the MITEQ amplifier discussed in the text. (b) MITEQ amplifier noise figure as a function of microwave input power for various frequencies of dc field modulation.

VI. Further signal enhancement techniques.

While the configuration described in Section IV if implemented could directly provide useful data at diamond anvil cell pressures, we would like to develop new techniques to increase the microwave signal from the sample. Based on a general microwave spectroscopy signal analysis the most efficient way to increase the signal is to increase what is termed the filling factor. The filling factor is proportional to the ratio of the sample volume to that of the entire resonant structure. For a sample that fits inside the hole in the diamond anvil pressure gasket, and our dielectric TE 101 cavity (as shown in Fig. 3), this corresponds to a filling factor of only 10^{-4}. Clearly there is much room for improvement, and we have considered three approaches which we briefly discuss.

(1) microwave transmission through the hole in the pressure gasket
(2) develop a gasket with an intrinsic resonant mode
(3) utilize one of the diamonds as the entire cavity

We have taken some data for approach (1) whereby we utilized the metal pressure gasket from our diamond anvil cell as the wall between a pair of resonant cavities quite analogous to our earlier work in transmission ESR. Utilizing a spin resonant sample (DPPH) inside the hole in the gasket we found that we could easily detect the resonant absorption, and this procedure may be worth further evaluation. It does have the additional demands of a dual resonant system, although we know how to solve that problem from our past experiences.

Approach (2) is in principle the way that could result in the highest filling factor, but we are not convinced that a suitable self-resonant mode of the "washer" type gasket can be found. This approach has been previously reported,[3] but the authors encountered numerous problems due to dimensional changes in the resonator when cooled to low temperature. Personal conversations with one of the authors led us to conclude that the problems with that approach would be difficult to overcome. We intend to first pursue the feasibility of this approach via theoretical and numerical analysis, possibly with the help of undergraduate physics majors in an independent study program.

The third approach is one that definitely can be implemented, and should result in at least an order of magnitude increase in filling factor. However, it also has some new demands due to the need for a much higher microwave frequency (corresponding to the smaller resonant cavity volume). It would also require developing an efficient means of coupling to this resonant cavity.

In summary, the system developed as described in Section IV should provide useful high pressure data (up to ~100 kbar) if implemented. We believe we could do this with a graduate student and some modest support. We will seek such funding and also continue to investigate means to substantially increase sensitivity along the lines discussed in Section VI.

References:

1. J. D. Barnett, S. D. Tyagi, and H. M. Nelson, Rev. Sci. Instrum. **49**, 348 (1978).
2. Mark W. Coffey and John R. Clem, Phys. Rev. Letts., **67**, 386 (1991).
3. N. Sakai and J. H. Pifer, Rev. Sci. Instrum. **56**, 726 (1985).