## US Navy's Superconductivity Programs Scientific Curiosity to Fleet Utility

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Abstract-The US Navy's interest in superconductivity began shortly after World War II when programs at the Naval Research Laboratory (NRL) and the Office of Naval Research (ONR) began exploring the science of superconducting materials. Throughout the 1950's and 1960's these programs discovered new superconducting materials and added much to the basic understanding of the phenomena. Technology development programs began in the late 1960's with major efforts and ONR, NRL, and the Navy's Warfare Centers. Development of superconducting quantum interference devices (SQUIDs) used to detect underwater mines and submarines began at the Warfare Center in Panama City, FL in 1969. At the same time scientists and engineers at the Warfare Center in Annapolis, MD began their own technology efforts to develop quiet, high power density ship propulsion motors. ONR and NRL expanded their programs to include superconducting electronics as well as efforts to develop technologically useful materials (films and wires) for the Navy's technology programs.

The Navy's superconductivity efforts accelerated rapidly after the discovery of high temperature superconducting (HTS) materials. A major effort led by NRL developed and launched HTS electronic devices and subsystems into space. The Navy Warfare Center in San Diego and ONR/NRL began programs developing low loss filters for electronic communications as well as the development of fast, low power superconducting digital devices. Navy scientists led industrial programs for development of full scale HTS ship propulsion motors and HTS filters for communication systems. As the 21<sup>st</sup> century began, the Navy started to develop superconducting systems for fleet implementation. The first ship to use a superconducting system was the USS Higgins that uses superconducting cables in a degaussing system (2008).

#### Part 1. Naval Research Laboratory\*

### **1948-1967: The beginning**

Interest in superconductivity for the Navy began at NRL circa 1948 in the Cryogenics Branch, headed by Dr. Richard L. Dolecek, of the Electricity Division, headed by Dr. Jules DeLauney. These two individuals published the first NRL scientific article on superconductivity in 1947 – "Superconductivity and the Debye Characteristic Temperature<sup>1</sup>". In the same year,

NRL hired Dr. Warren Henry<sup>2</sup> to build a high magnetic field laboratory similar to the Francis Bitter design and bought one of the first commercially sold Collins helium liquification facilities (Collins liquefier Experimental work on low temperature techniques and instrumentation, and both theoretical and experimental research on magnetic and superconducting properties of materials at low temperatures were being investigated<sup>3-5</sup>. Two years later (1950), the Cryogenics Branch hired Robert A. Hein to begin studies on superconducting materials at temperatures below 1 K. To do this, Hein set up an adiabatic demagnetization refrigerator, which used the high magnetic field facility at NRL, and liquidhelium-cooled magnetic salts to cool samples from 1.2 K to about 0.01 K. Hein's ultralow temperature facility was unique in the United States with respect to the ease of use and turnaround time between experiments. Hein used this uniqueness to foster many collaborations with industrial and university scientists to advance his own research over the next 20 years. The availability of high magnetic fields, liquid helium, low temperature instrumentation, dedicated laboratories, an ultralow temperature facility, and a competent interacting group of scientists made the cryogenic group at NRL one of the strongest low temperature physics groups in the world.



Fig. 1. (Left) Dr. Warren Henry performing research at cryogenic temperatures in NRL's high magnetic field facility demagnetization (Right) Dr. Robert Hein using adiabatic demagnetization to test the properties of superconducting materials at temperatures to 10 mK.

During much of the next two decades, Hein established an international reputation for his work in superconducting materials. Among the many accomplishments during this period of time was the

discovery of superconductivity in tungsten<sup>6</sup> (Tc = 0.015 K), iridium<sup>7</sup> (Tc = 0.10 K), and the compound germanium-tellurium<sup>8</sup> (GeTe) at temperatures near 0.3 K. This later discovery in 1964 takes on great historical significance since it was the first low-carrier-concentration superconductor ever found and represented a confirmation of a theoretical prediction made in 1964.

#### 1967-1986: Expansion of effort

Interest in superconductivity was growing worldwide with expectations of its applied use for power applications, such as ship propulsion systems, and for electronic applications, such as high speed computers or sensitive magnetometers. A decision was made to expand the NRL effort in superconductivity with a focus on Navy relevance. Dr. Donald U. Gubser was hired in 1969 to build a dilution refrigerator and continue basic research in superconducting materials at ultralow temperatures. Dr. Stuart A. Wolf was hired in 1971 to develop a superconducting thin film synthesis facility and Dr. Martin Nisenoff followed in 1972 to head a group focused on SQUID magnetometry. A new Branch was formed in 1971 with Dr. Hein as branch head and rapidly moved into new areas.



Fig. 2. (Left) Don Gubser with dilution refrigerator (Right) Stu Wolf with sputtering system

Throughout this period, the decade of the 1970s and early 1980s, work continued on the more basic aspects of superconductivity<sup>9</sup>, e.g. magnetic flux motion in pure superconductors<sup>10</sup>, the effects of pressure on the superconducting state<sup>11</sup>, and the effects of neutron radiation on magnetic flux pinning were all explored<sup>12</sup>. The group also continued to search for new superconducting materials. Among the new classes of materials studied for superconductivity were ternary alloys<sup>13</sup>, and organic materials<sup>14</sup>. The dilution refrigerator largely replaced adiabatic demagnetization for conducting ultralow-temperature research. A major focus of the superconducting materials effort was directed to studies of dimensionality effects in superconductivity. Drs Wolf and Gubser pioneered a new superconductivity subfield by hosting a conference called "Inhomogeneous Superconductors" (1979)<sup>15</sup> at a West Virginia retreat

where they presented early results on ultrathin, granular NbN superconductors. There were major theoretical and practical concerns about how thin a material could be and remain superconducting and what the exact nature of the superconducting state (topological phase transitions) was as this limit was approached <sup>16</sup>.

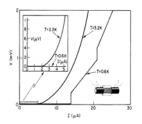




Fig. 3. (Left) Granular film 2D transition (Right) SQUID Magnetomertry workshop: Coolfont Conferences

On the synthesis side, Wolf set up a thin film fabrication facility that produced superior niobium and niobium nitride superconducting films. With the fabrication and processing facility in place, Wolf and Nisenoff began making Josephson junctions, superconducting quantum interference devices (SOUIDS), and other electronic devices and began to participate in national programs on applied superconductivity. During this period Drs. Gubser, Wolf, and John Claassen began active collaborations with the Naval Coastal System Center (NCSC), in Panama City, Florida to investigate noise in the SQUID system<sup>17</sup> that was undergoing field testing. In a collaborative project with David Howe in the metallurgy group at NRL, synthesis and processing and characterization of V<sub>3</sub>Ga wire also began in the 1970's and continued into the mid 1980s. Drs Howe, Francavilla, and Gubser, reported on some of the best  $V_3$ Ga wire ever produced using an alloyed core bronze technique<sup>18,19</sup> during this program.



Fig. 4.(Left) Clif Krowne, Ed Cukauskas, and Marty Nisenoff (Right) Tom Francavilla

Systems development also took place in this time frame. In a joint effort with the Communication Sciences group at NRL, SQUID magnetometers were developed as a compact receiving antenna for the ELF transmissions. The three axis magnetometer system was designed and

tested to be operation while on a moving platform which would be submerged in 100 meters below the surface of the ocean off the coast of San Clemente Island, California<sup>20,21</sup>.

In 1979 the Cryogenic and Superconductivity Branch moved to the Electronic Division and then was disestablished following Dr. Hein's retirement. Applied electronic efforts, headed by Dr Nisenoff remained in the Electronics Division, while the materials efforts, with Drs. Gubser and Wolf, was merged with the Metal Physics Branch in the Materials Division. The electronic efforts expanded to include digital circuitry, and passive superconducting microwave devices. Dr. Nisenoff began to be more involved with cryogenic refrigeration necessary for superconducting applications and was assigned part time to ONR to assist Mr. Edelsack with the superconductivty and cryogenics program. Dr. Edward Cukauskas worked on developing alternative barriers of the niobium tunnel junctions and had a very productive collaborative program on this topic with the industry. Dr. John H Claassen worked on the detection of microwave radiation with superconducting devices and in exploring microwave passive circuit elements based on the kinetic inductance property of the superconducting state.

The theoretical effort on superconductivity at NRL was started in 1973 by Barry Klein and Dimitrios Papaconstantopoulos who, using band structure calculations, implemented a methodology for calculating superconducting properties from first principles. In 1974 they published their first PRL, demonstrating a quantitative evaluation of the electron-phonon coupling and superconducting transition temperature for the transition metals V and Nb, and for NbC. In the fall of 1974, Larry Boyer joined the group and in the next four years the trio performed a series of calculations of the electronic structure and superconducting properties of many different classes of materials, i.e. carbides, nitrides, hydrides, and A15 compounds. A study of superconductivity for 32 elements<sup>22</sup> in the periodic table was done in collaboration with an IBM group as well as published calculations on the A15 compounds that pushed the computational capabilities of the times<sup>23</sup>. Other papers on the interpretation of superconductivity in palladium hydride and the accompanying inverse isotope effect; and the first quantitative prediction of high superconducting temperature in metallic hydrogen were done in this period. In late of 1979 Warren Pickett joined the theory group and together with Klein, Papa and Boyer performed calculations on a few C15 laves phase compounds as well as on transition-metal nitrides. In 1984 they published a paper in Nature<sup>24</sup> with a result that MoN might have a superconducting transition temperature of 30K, a record for that time. Unfortunately,

the experimentalists at NRL and elsewhere could not fabricate the material in a stoichiometric B1 structure. In 1988 Boyer and Michael Mehl, working with Henry Krakauer of William and Mary showed, via calculations of the elastic constants that a phonon instability prevents the formation of pure MoN.



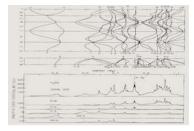


Fig. 5. (Left) Dimitri Papacontantopoulous, Warren Pickett, Barry Klein, and Larry Boyer (Right) Typical Band Structure Diagram.

An important event of the superconductivity efforts at NRL during this era was the organization of the 1986 Applied Superconductivity Conference<sup>25</sup>. The chairman of this conference was Mr. Edgar Edelsack, who ran the superconductivity program at ONR, but cohosts and co-organizers were the NRL trio of Drs. Gubser, Wolf, and Nisenoff from NRL. Together, ONR and NRL successfully hosted this international conference in Baltimore, Maryland, where the theme centered on the 75th anniversary of the discovery of superconductivity. The tone of the meeting was reflective of past accomplishments. No one at the meeting suspected that the field of superconductivity was about to accelerate in a manner of extraordinary proportions.

# 1987 – 2010 High Temperature Superconductivity Days

NRL was well positioned to respond to the challenge of the new HTS discovery. More than 30 scientists became actively involved in HTS research and quickly established NRL's reputation as a major laboratory in the field. By March of 1987, NRL had isolated, identified, and established processing procedures for the first superconducting material with a transition temperature Tc over 90 K<sup>26</sup>. Later, NRL researchers made a wide range of contributions including: determination of the phonon density of states in YBCO<sup>27</sup>, Raman spectroscopic investigations that revealed the novel symmetry of the superconducting order parameter in both n-type and p-type cuprate high temperature superconductors<sup>28</sup>, high resolution structure studies of inhomogeneities in HTS materials, <sup>29</sup> the discovery of several new superconductors with Tc above 100K,<sup>30</sup> the discovery of an anomalous temperature dependence of

 $H_{c2}$  in  $Bi_2Sr_2CuO_6$ ,  $^{31}$  measurements of the pressure dependence of  $T_c$  for HTS materials,  $^{32}$  synthesis of thin films of HTS using pulsed laser deposition,  $^{33}$  measurements of the magnetic penetration depth and microwave losses in a YBCO/LaAlO3/YBCO trilayer transmission line,  $^{34}$  casting of BISCCO,  $^{35}$  Synthesis of YBCO thin films with low microwave surface resistance using CVD,  $^{36}$ , optical detection in thin granular films of YBCO,  $^{37}$  thermo-electric power in YBCO,  $^{38}$  the synthesis of dense  $MgB_2$ ,  $^{39}$  and the development of a contactless method to determine the  $J_c$  of thin film superconductors.  $^{40}$  During this time period they also developed a method for determining the transport spin polarization of ferromagnetic materials using point contact Andreev reflection (PCAR).  $^{41}$ 

In the leadership category, NRL was also in the forefront of the HTS phenomena. NRL organized two of the first international conferences on HTS materials (Materials Research Society (MRS) Special Symposium (Gubser, April 1987) and "Novel Mechanisms for Superconductivity" (Wolf, June 1987)). The Chief of Naval Research formed the Naval Consortium for Superconductivity in August 1987, which became the official body for overseeing the Navy's superconductivity program (Gubser, chairperson). NRL scientists became managers of the new SDIO program of HTS applications (Gubser, Nisenoff), and primary consultants on the new DARPA HTS program (Wolf). A new NRL program in basic research on HTS materials was started (Gubser, Wolf, Nisenoff, Klein), and an existing ONR program on superconductivity (Nisenoff) was refocused on the new materials. Gubser, Wolf, and Nisenoff participated in many national study boards to help plan a national response to the rapidly growing field.

Perhaps the most important NRL superconductivity program during the 1990's was on space applications of superconductivity. This program, called the NRL High Temperature Superconductivity Space Experiment (HTSSE), is the most aggressive program in the world on promoting systems applications of superconductivity... The first phase of HTSSE was to obtain simple HTS devices in 1991, just 4 years after the discovery of these materials, from about 23 different research organizations, which were then testeded and space qualified by the NRL Center for Space Technology. In the second phase of the HTSSE program, 11 fully functional microwave components and sub-systems were procured or built and, then fully space qualified and mounted on a scientific payload ARGOS which as launched in1999. These devices were monitored for more than 3 years in orbit before the program was terminated. This program was nationally touted for fostering industrial competitiveness in the area of superconducting microwave devices<sup>42</sup>.



Fig. 6. (Left) Post of HTSSE devices (Right) M. Nisenoff, S. Wolf, J. Ritter, and G. Price – Technical leaders of the HTSSE project

When the high-temperature superconductors came on the scene the theoretical effort was at the forefront of the frenetic research. The NRL theoretical team, now joined by David Singh and Ronald Cohen, published a series of seminal PRB and PRL papers on the electronic structure of these materials. Of particular note are two review articles by Pickett, one on High Tc cuprate superconductors<sup>43</sup> and another establishing a Fermi surface for the high temperature superconductors<sup>44</sup>. Other important contributions were studies by Pickett and Singh on the borocarbide superconductors, and a Science article by Pickett and Steve Erwin on K3C60<sup>45</sup>. After the departure of Pickett for UC Davis in the mid-nineties Singh had several key papers on the electronic structure of many other materials including ruthenates and cobaltates. In 1996 Igor Mazin joined the group and participated in several projects with Singh receiving a lot of attention from both the electronic structure and superconductivity communities. Mazin working with Jens Kortus and Boyer produced an outstanding PRL<sup>46</sup> on MgB2, a 40K superconductor, which was explained by Mazin et al and other groups as a good example of electron-phonon mechanism. More recently Mazin joined by Michelle Johannes started work on the new Fe-based superconductors, the so-called pnictides, continuing the NRL tradition of significant publications in PRL<sup>47</sup>.



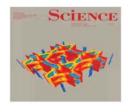


Fig. 7. (Left) L. Boyer, J. Serene, W, Pickett, J. Cohen, and D. Singh (Right). Fermi level diagram of YBCO  $\,$ 

As the century turned, the experimental research efforts at NRL focused more and more on the characterization of HTS wires and tapes for use in power systems. Two main thrusts were: mechanical strength<sup>48-50</sup> and durability, and electrical loss<sup>51</sup> during ac operation. These projects were closing tied with industrial efforts and the mechanical specifications for the HTS synchronous motors built by industry (American

Superconductor Corporation) were set by the experimental results of Dr. Ronald Holtz.



Fig. 8. (Left) Ron Holtz (Right) Mike Osofsky

Superconductivity has been a major program at NRL for over 60 years. The present effort traces its history to the earliest beginning in 1948. The people and their many accomplishments have kept superconductivity research strong at NRL. In 2010 NRL continues exciting research in basic (experimental and theory), and applied (electronic and power) research and development in superconductivity.

\* Contributions for other Navy organizations will occur in subsequent issues of the IEEE Transactions of Applied Superconductivity

#### References

- 1. J. DeLaunay and R.L. Dolecek, Phys. Rev. <u>72</u> 141 (1947)
- 2. W. E. Henry, "Lectures Notes in Physics" Magnetic Phenomena 337 10 (1989)
- W. E. Henry, and R. L. Dolecek, Rev. Sci. Instru. <u>21</u> 496 (1950)
- 4. J.R. Clement, and E.H. Quinnell, Rev. Sci. Instru. <u>23</u> 213 (1952)
- 5. J. DeLaunay, Phys Rev. <u>79</u> 398 (1950)
- 6. J.W. Gibson, and R.A. Hein, Phys Rev Letts <u>12</u> 688 (1964)
- 7. R.A. Hein, J.W. Gibson, B.T. Matthias, T.H. Geballe, and E. Corenzwit, Phys. Rev. Letts. 8 408 (1962)
- 8. R.A. Hein, J.W. Gibson, R. Mazelsky, R.C. Miller, and J.K. Hulm, Phys. Rev. Letts <u>12</u> 320 (1964).
- 9. D.U. Gubser, Phy Rev B 3 827 (1972).
- 10. S. Wolf, D Gubser, and D. E. Farrell, Solid State Comm. 14 457 (1974)
- 11. A.W. Webb, D.U. Gubser, and L.C. Towle, Rev. Sci Instrum. <u>47</u> 59 (1976)
- 12. T.L. Francavilla, B.N. Das, D.U. Gubser, R.A. Meussner, and S.T. Sekula, J. Nuclear Matls. <u>4</u> 377 (1977)
- 13. D.U. Gubser and R.A. Hein, Solid State Comm. <u>15</u> 1039 (1974).
- D.U. Gubser, w.w.Fuller, T.O. Poehler, D.O. Cowan, M. Lee, R.S. Potember, L.Y. Chiang, and A,N. Bloch, Phys Rev B <u>24</u> 478 (1981)
- 15. "Inhomogeneous Superconductors" Edited by D.U. Gubser, T.L. Francavilla, J.R. Leibowitz, and S.A. Wolf AIP conf Proc. No. 58 (1979)

- 16. .A. Wolf, D.U. Gubser, and Y. Imry, Phys. Rev. Letters 42, 324 (1979).
- 17. J. H. Claassen, S.A. Wolf, and D.U. Gubser, IEEE Trans. MAG-21, 434 (1985)
- 18. D.G. Howe, D.U. Gubser, and T.L. Francavilla, IEEE Trans. MAG-17, 654 (1981)
- D.U., Gubser, T.L. Francavilla, D.G. Howe, R.A. Muessner, and F.T. Ormand, IEEE Trans on Magnetics MAG-15 385 (1979)
- 20. S.A. Wolf, J.R. Davis, and M. Nisenoff, IEEE Trans Comm. COM-22549 (1974)
- 21. J.R. Davis, R.J. Dinger, and J Goldstein, NRL Report 7990, April 9 (1976)
- 22. D.A. Papaconstantopoulos, L.L. Boyer, B.M. Klein, A.R.Williams, V.L. Moruzzi, and J.F. Janak, Phys Rev B15 4221 (1977)
- 23. B.M. Klein, L.L. Boyer, and D.A. Papaconstantopoulos, Phys. Rev B18, 6411 (1978)
- 24. D.A. Papaconstantopoulos, W.E. Pickett, B.M. Klein, and L.L. Boyer, Nature 308 494 (1984).
- 25. IEEE Trans on Magnetics MAG-23 (1987).
- 26. S.B. Qadri, L.E. Toth, M. Osofsky, S. Lawrence, D.U. Gubser, and S.A. Wolf, Phys Rev **B 35**, 6868 (1987)
- 27. J.J. Rhyne, D.A.. Neumann, J.A. Gotaas, F. Beech, L. Toth, S. Lawrence, S.A. Wolf, M. Osofxky, D.U. Gubser, Phys Rev. B 36 2294 (1987)
- 28. C. Kendziora, R. J. Kelley, and M. Onellion, Physical Review Letters, 77, 727 (1996).
- E. F. Skelton, A. R. Drews, M. S. Osofsky, S. B. Qadri, J. Z. Hu, T. A. Vanderah, J. L. Peng, and R. L. Greene, Science 263, 1416 (1994)
- 30. M. S. Osofsky, W. L. Lechter, L. Toth, E. F. Skelton, A. R. Drews, C. C. Kim, B. Das, S. B. Qadri, A. W. Webb, and R. J. Soulen, Jr., J. Supercond. **8**, 511 (1995); W. L.
- 31. M.A. Osofsky, R.J. Soulen, S.A. Wolf, J.M. Broto, H.Rakoto, J.C. Ousset, G. Coffe, S. Askenazy, P. Pari, I. Boozovic, J.N. Eckstein, and G.F. Virshup, Physical Rev. Lett, 71 2315 (1993)
- 32. D. D. Berkeley, E. F. Skelton, N. E. Moulton, M. S. Osofsky, W. T. Lechter, V. M. Browning and D. H. Liebenberg, Phys. Rev. B 47, 5524 (1993)
- J.S. Horwitz, D.B. Chrisey, M.S. Osofsky, K.S. Grabowski, and T.A. Vanderah, J. Appl. Phys. **70** (2) 1045(1991); D.B. Chrisey, K.S. Grabowski, M.S. Osofsky, Physica C **162-164**, 129 (1989)
- 34. J. M. Pond, K. R. Carroll, J. S. Horwitz, M. S. Osofsky, and V. C. Cestone, Appl. Phys. Lett. **59** (23) 3033 (1991)
- 35. B.N. Das, L.E. Toth, R.J. Rayne, B.A. Bender, M.S. Osofsky, R.J. Soulen Jr., W.L. Lechter, N.C. Koon, S.A. Wolf; Journal of Superconductivity **2** (2), p. 253 (1989).
- W. J. DeSisto, R. L. Henry, H. S. Newman, M. S. Osofsky, and V. C. Cestone, Appl. Phys. Lett. <u>60</u> (23), 2926 (1992);
- 37. M. Leung, P.R. Broussard, J.H. Claassen, M. Osofsky, S.A. Wolf, U. Strom, Applied Phys. Lett. <u>51</u>, 2046 (1987).

- 38. J. L. Cohn, S. A. Wolf, V. Selvamanickam, and K. Salama, Phys. Rev. Lett. 66, 1098 (1991).
- 39. H. N. Jones, C. R. Feng, M. Osofsky, E. E. Carpenter, and Cooper, IEEE Trans. On Appl. Supercond. <u>13</u>, 3056 (2003).
- 40. J. H. Claassen, M. E. Reeves, and R. J. Soulen, Jr., Rev. Sci. Instr, **62**, 996 (1991).
- R. J. Soulen, Jr, J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, P. R. Broussard, C. T. Tanaka, J. Nowak, J. S. Moodera, A. Barry, J. M. D. Coey, Science 282, 85 (1998).
- 42. T.G. Kawecki, G.G.Golba, G.E. Price, V.S. Rose, and W.J. Meyers, IEEE Trans.on Microwave Theory and Techniques, 44, 1198 (1996).
- 43. W.E. Pickett, Rev. Mod. Phys. <u>61</u>, 433 (1989)
- 44. W.E. Pickett, H. Krakauer, R.HG. Cohen, and D.J.Singh, Science 255, 46 (1992).
- 45. S.C. Erwin and W.E. Pickett, Science <u>254</u> 842 (1991)
- 46. J. Kortus, I.I. Mazin, K.D. Beleshchenko, V.P. Antropov, and L.L. Boyer, Phys Rev. Lett. <u>86</u> 4656 (2001)
- 47. I.I. Mazin, D.J. Singh, M.D. Johannes, and M.D.Du Phys. Rev. Lett. <u>101</u> 057003 (2008
- 48. R.L.Holtz, 2009 NRL Review, pp.180-182, (Naval Research Laboratory, Washington DC, 2010).
- 49. J.M.Wolla, R.L.Holtz and J.P.Voccio, IEEE Trans. Appl. Supercond., <u>17</u> 3050 (2007)
- 50. R.L.Holtz, IEEE Trans. Appl. Supercond., <u>11</u> 3238 (2001).
- 51. Soulen RJ, Osofsky MS, Patten M, et al.IEEE Trans. Appl. Supercond. <u>15</u> 2381 (2005)