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Why I Haven't Retired

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Keywords

Abstract

What is written below is, as requested by the editor of *AR Condensed Matter Physics*, a set of recollections and insights gained from my personal trajectory that starts from my earliest years and continues on until now. I have been a participant in the growth of solid state physics from its early quantum insights to the highly popular foci of today's vibrant condensed matter science community, while working at three institutions that helped spearhead this growth—UC Berkeley, Bell Labs, and Stanford University. It is rare to be actively involved in any creative enterprise for more than six decades. I credit my good fortune to stimulating science; great students and colleagues; a happy home; warm friendships; and, evidently, to my having inherited good genes.

SCHOOL YEARS

I grew up in San Francisco in a thriving middle-class family that had some appreciation for science. My grandfather left Posen as an 18-year-old because, he told me, "as a Jew I couldn't become an officer in the Prussian army." While taking me during my school days to an open house event at Lick Observatory he recounted how he had taken his bride there by horse and buggy on their honeymoon. My aunt, Pauline Geballe, a high school chemistry teacher in Portland, was very proud of Linus Pauling and several other "distinguished former students" of hers. She taught me my first chemistry lesson in my preschool days: "Johnny was a chemistry student. Johnny is no more, for what he thought was H_2O, was H_2SO_4." But my real interest in science was sparked by my brother Ron, two years my senior. He was a great reader and a born teacher. I used to play with his chemistry set and remember starting a couple of scary fires. We listened to a crystal radio set from the World War I era that we tuned randomly by scratching the "cat's whisker" (a metallic spring) over the surface of a black crystal (probably PbS). That mysterious happening was my first encounter with solid state physics, although I don't recall trying to figure out how it worked.

COLLEGE DAYS: 1937–1941

I graduated from Galileo High School, a place where recent graduate Joe DiMaggio hitting balls meant more than Galileo Galilei dropping them. I went "east to college," i.e., took the ferryboat across the bay to Berkeley. (The Bay Bridge opened the same year.)

My attempt to measure what I called the heat of vaporization of electrons from a tungsten filament, i.e., the work function, as a special research project that I chose in my junior-year physical chemistry lab, failed—what I had learned in thermodynamics didn't include space-charge potentials. But I also found out that a failed experiment is not necessarily bad, because it stayed in my mind. When I met Boris Moyzhes much later as an emeritus professor he told me of an energy-efficient way of reducing the space charge. That led to our proposing an idea for an efficient thermionic heat engine (1). Further advances, including some experimental verification (J. Mannhart, T.H. Geballe, et al., unpublished data), demonstrate that a highly efficient transformation of heat into electrical power may well be realized.

My enthusiasm for research regardless of that failed attempt was recognized by Bill Forysthe, the laboratory TA, and led to my measuring the heat capacity of gold in Professor William Giauque's lab during my senior year. Giauque's pioneering investigations of the third law of thermodynamics needed more accurate inputs for lattice heat capacities than were provided by Debye's theory that predicted a simple T-cubed behavior dependent upon a single characteristic constant. Giauque hoped to stimulate the development of a more accurate Born-von-Karman-type theory by providing a systematic data set of the low temperature–specific heat of fcc metals (2). He had just purchased a chunk of gold from prize money, and I was offered the opportunity to measure its heat capacity using apparatus and procedures that were already in place. "Theories can come and go," he told me, "but accurate experimental results can be forever."

I learned from Giauque's comprehensive notes, handwritten on sheets of worn yellow paper, how to measure radiation losses and minimize sources of error. Low-temperature research then was done in a few places only; techniques were learned in an apprentice-like fashion. The introduction of the Collins helium liquefier after World War II changed all that; cryogenic temperatures are routine today and data are collected automatically. But just as something is lost when letter writing is supplanted by texting, so something is lost by not observing what is

happening in real time. Giauque's notes have been resurrected and are worth reading (3). During the all-night runs, which required continuous data taking, I was sustained by the thought, following from Giauque's comment, that I might be obtaining results that would last forever (4). . .and also by timely milkshakes brought to me by an English major girlfriend who would soon become my wife.

WORLD WAR II: 1941–1945

My research came to an abrupt end. Shortly before the United States entered the war, I was called to active duty in the US Army Ordnance Department and was sent overseas to the South Pacific. I spent the next four years in Australia, New Guinea, and the Philippines as an army ordnance officer responsible for maintaining guns. In the later stages of the war, boxes containing equipment to replace the antiquated mechanical devices that were being used to direct antiaircraft artillery arrived from a place labeled Bell Laboratories. Perhaps if those boxes had also come with instruction manuals, we might have won the war sooner.

GRADUATE SCHOOL: 1945–1950

By the time I was discharged, more than four years after I had left Berkeley, I was tempted to get on with life and raise a family. But the lure of research was tempting, and with encouragement from my wife I accepted Giauque's offer to go on to graduate school. Two more seniors, Dave Lyon and Jim Fritz, were planning to study the spin ordering of transition-metal ions in hydrated paramagnetic salts and had upgraded the adiabatic demagnetization apparatus used by Giauque and MacDougall in their pioneering experiments (5). That frontier research was exciting. I went off to the library to search for an interesting salt and chose $CuSO_45H_2O$, partly because Cu^{++}, with only one unpaired electron, looked simple, and partly because its crystal structure had previously been determined (6). I started my research career studying copper sulfate and am ending it studying copper oxide.

    I had no idea how to grow the large single crystal that would be needed. Giauque suggested I write to Mervyn Kelly, the President of Bell Labs, and ask him. I soon received a five-page letter from Alan Holden with detailed instructions that he later published in the *Transactions of the Faraday Society*. I followed them and grew a 1,400-gram single crystal. Professor A. Pabst helped me align it in a pantograph device so that it could be ground into an ellipsoid whose major axis was parallel with the axis of maximum magnetic susceptibility (7).

    Giauque, as a young faculty member in 1924, had calculated from susceptibility data of $Gd_2(SO_4)_3 \cdot 8H_2O$, measured at Leiden, that temperatures below 1 K could be reached by an isentropic, i.e., reversible adiabatic, demagnetization from above 1 K. The expression he used was later obtained in closed form by Leon Brillouin and has become known as the Brillouin function.

    To avoid dehydrating the $CuSO_45H_2O$ crystal, I decided to build a calorimeter out of plastic that could be sealed without heating. I finally succeeded in making one that had no superfluid leaks (8), but I don't think plastic calorimeters have been used since, and I know why. Temperatures below 1 K calculated from the thermodynamic definition $T = \Delta S/\Delta Q$ showed that only one-half of the Rln2 entropy of the Cu spin 1/2 ions had been removed by the 8,000 gauss field (9). The structure had two different Cu sites with different Cu-O distances, which led me to conclude that only one of the sites had been polarized. But it wasn't until after I turned in my thesis in 1949, the same year that Giauque won the Nobel Prize, that I realized the result was a natural outcome of superexchange.

Giauque obtained the resources to build a much more powerful demagnetization system, and I was tempted to stay on as a postdoc and investigate the remaining entropy. The experiment was eventually carried out in fields of up to 90 T (10). However, I didn't stay because of a special course given by Charles Kittel, who was visiting from Bell Labs. It opened the vistas of solid state physics to me, broadening the chemical thermodynamics perspective to which I had been previously exposed. The informative notes that he handed out later became the first edition of his *Solid State Physics* text (now in its eighth edition). I went to a seminar Homer Hagstrum gave during Christmas vacation and asked him about some ongoing research at Bell that I had learned about in Kittel's course. I soon got a letter inviting me back to Bell—there was no formal recruiting then; it was by word of mouth.

BELL LABS: 1952–1975

Semiconductors

I went to Bell and was overwhelmed by the scientists and the science emerging three years after the invention of the transistor. When I was offered a staff position with the promise that I could choose my own research project, it seemed too good to be true. It wasn't! I prepared my four-year-old son for the trip east by telling him that the best toy store in the world was in Summit, NJ. Later, as we drove by the long linear research building at Murray Hill Labs he shouted, "That's not Giauque's lab. That's Daddy's lab." Not quite true, but from the very start I felt very much a part of the place. Multidisciplinary research was common at Bell well before that practice became normal. I learned many things just from chance encounters in the long corridor going to lunch in one direction or going to the library in the other. It was customary for experimental staff to have one technical assistant. I was lucky to have George Hull. He was careful and skilled and had a strong interest in the research itself.

There probably will never again be another organization like the Bell Labs of that era. It was the research arm of AT&T, a closely regulated monopoly. Research was well supported because there were strong financial incentives for improving productivity, and the long-term horizon gave undirected research the recognized potential for doing just that. There was no need for evaluations by outside visiting committees or numerous support letters for hiring. Decisions were made by the staff scientist in consultation with administrators who, like Joe Burton, Bruce Hannay, and Sid Millman, my three bosses during my time at Bell, were themselves excellent scientists. They contributed insightful contributions to my research as well as buffered me from administrative chores so that my time was free for research.[1] Staff members were "innocent until proven guilty," meaning research was expected to be good, and accordingly it was supported. In the few instances that proved otherwise, it was possible to arrange a graceful exit, because of the large size of the company. We lived in a rich, conservative, and stuffy part of New Jersey where people had voted Republican for 100 years, corporate vice presidents commuted to Wall Street on the Lackawanna Railroad, stores were closed on Sundays, and real estate was quietly segregated. The Bell crowd was a different mix—we were young, uninhibited, and living away from our hometowns and families. Our social lives co-mingled with our scientific lives. The friendships we made were deep and lasting. When we scattered, particularly after the Bell System was broken, we stayed in contact. Today, alas, I too often read about those friends in the obituary columns.

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[1] An example: I happened to be peripherally involved with Bell's decision to not consolidate expertise in crystal growth into one department, as had been advocated by those seeking to improve crystal growth technology. The research benefited much more by keeping the crystal growers such as Joe Remeika intimately part of the ongoing research.

My first big decision in 1952 was whether to work on semiconductors in Joe Burton's chemical physics subdepartment or to work on superconductors with Bernd Matthias. Bernd tempted me. He quoted Fermi, who had urged John Hulm and him, when they were at the University of Chicago, to "search for new superconductors." That advice I think was based on the notion that patterns in the occurrence of superconductivity might produce valuable clues for theory and be the springboard for other significant discoveries. That assumption has motivated my teaching and research throughout my career. Bob White and I later gave a graduate course at Stanford that featured the properties of real materials as a way to introduce theoretical ideas. It grew into a book (11) that complements traditional literature and remains in use. I hope that some younger condensed matter physicists will produce an updated version along those lines.

However, I had trouble deciding between these two choices. Jim Fisk, then president of Bell Labs, said I could always change but that I should start with Joe, so I did; I never regretted it. I was rewarded with immediate access to a wealth of well-characterized single crystals and the golden opportunity to study their properties. My very first measurement, the thermal conductivity of pure silicon, done simply to check the apparatus at room temperature, produced a surprise. The thermal conductivity was a factor of two larger than the literature value. After eliminating all the errors I could think of, I arrived at the pleasant conclusion that the factor of two arose because the crystal I was given was much more perfect than what the previous state of the art had been able to produce. Chemical purity and perfection had been vastly improved in response to the needs of the new transistor technology. Interactions between science and technology provide a two-way street for advancing condensed matter physics, and indeed I have seen many such interactions throughout my career.[2]

I developed a plan to measure band gaps by comparing thermoelectric (Seebeck) voltages of judiciously chosen n- and p-doped semiconductors. I explained this idea to Conyers Herring when I first met him. He gently explained why my method wouldn't work. I tried to convince him otherwise, but failed. Nevertheless, I learned something. It's good to talk to theorists—but even if they tell you your experiments won't do what you think, it doesn't mean you shouldn't try.

That conversation with Conyers was the beginning of a cherished collaboration. He soon recognized immediately that the huge increases in the thermoelectric power of high-purity germanium we had found at low temperatures (12) could be due to low (with respect to thermal) energy phonons preferentially scattering electrons down the thermal gradient. This made a contribution to the thermoelectric power that was large compared with the normal kT/e term due to the diffusion of electrons. In addition, Herring's model predicted they should make a small but detectable contribution to the thermal conductivity. This added contribution to the Seebeck effect, known as phonon drag, had previously been predicted by Gurevich to make a small contribution to metals (13). Frederikse independently arrived at the same qualitative idea to account for similar increases he had measured in single crystals of germanium (14). Conyers, by a judicious transformation from thermal to isothermal transport using the Kelvin relation between the Seebeck and Peltier coefficients ($ST = \Pi$), found an expression that showed the "phonon-drag" phonons (i.e., those that make the largest contribution to the effect) have very long lifetimes and in the steady state are scattered out of equilibrium so that they contribute to the Peltier heat current. They can be studied at frequencies lower than the thermal energy scale ~kT,

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[2]An example: Impurity requirements went well beyond the norms of high-purity chemistry. In my first weeks in Burton's group I learned that transistors were failing due to an unknown "deathnium" that killed minority carrier lifetimes. Radiotracer studies soon identified it to be due to copper recombination centers present in parts per million. The copper came from a copper distillation column that had been installed in an ill-advised effort to increase output and to improve purity.

but much higher than those that can be generated in the laboratory by acoustic transducers (15). Realizing that changing the sample dimensions would change boundary scattering lifetimes of these long-lived phonon-drag phonons at temperatures where thermal phonons would be unaffected, we were able to verify his model by comparing the Seebeck effect and the thermal conductance of identical samples with different cross sections (16). We developed a sensitive method for doing this by using a tuning fork geometry prepared from a single crystal of germanium that had arms with different cross-sectional areas. We avoided having to measure temperature gradients absolutely by simply relying on the more accurate energy inputs that were needed to keep the gradients along the arms identical. This was accomplished within 0.001 K by tuning the thermoelectric voltage of a germanium bridge anchored across the upper ends of the two arms to zero while the single crystal itself assured that lower ends at the base were at the same temperature.

The unprecedented control over doping made it possible for us to investigate many other transport properties. We were able to measure absolute electron mobilities to better than 10% from the fractional changes in magnetoresistance and upon application of uniaxial stress (17). It was also possible to test the proposal of Pomeranchuk (18) that fluctuations in mass due to random distribution of naturally occurring isotopes could cause inelastic phonon scattering. We verified his idea directly by finding that the maximum thermal conductivity of a 95.8% Ge74-enriched sample was three times greater than one with the normal isotopic content (19). However, this sizeable increase was still less than the 15-fold increase expected from theory (20). The reason soon became apparent when a strong dispersion in the transverse acoustic branch was revealed by inelastic neutron scattering. Much later, in an experiment at the General Electric Research Laboratory based on the same physics, diamond crystals depleted of carbon 13 were found to have the highest thermal conductivities of any known material, and consequently to have an unusually high resistance to damage by ultraviolet radiation (21).

Not surprisingly, the phonon-drag contribution saturates upon increasing the concentration of carriers. However, we found an unexpected sign reversal of the Seebeck voltage at low temperatures when the doping concentration was not quite high enough (for Si $\sim 2 \times 10^{18}$ cc^{-1}) to cause degeneracy (16). This suggested a model where the mobile carriers condense back onto their dopant parents, which are close enough together to form a narrow impurity band, slightly compensated because of a small concentration of minority dopants that is always present. I suspected this reversal in sign that occurred in both n and p-type samples could be due to the nearly filled impurity band if it were to contain only one state per wave-vector value. I found support for this idea by showing that there is no reversal in the sign of the Seebeck coefficient when minority dopants are deliberately added to increase the compensation to $\sim 90\%$, thus nearly emptying the impurity band. However, that interpretation got nowhere because no one believed there could be a band with only one state per carrier. Later, Hubbard showed that when large local correlations, parameterized by the Hubbard interaction, U, are greater than the original band width, W, the band splits into upper and lower bands (22), thus supporting our interpretation of the experiments.

For even lower dopant concentrations (in the range $\sim 10^{16}$ cc^{-1}), the dopants are too far apart to form an impurity band. Mike Pollak and I, following a suggestion by Phil Anderson, found that when the majority carriers had condensed back onto their parent sites, the frequency-dependent ac conductivity was orders of magnitude larger than the dc conductivity. This is due to the polarization caused by the hopping of majority carriers that are localized within the Coulomb field of a charged minority ion (23).

In even more lightly doped ($\sim 10^{14}$ cc^{-1}) high-purity crystals, the dopant sites do not directly interact with each other at all. Here, Hall and longitudinal resistance measurements were used to determine thermal activation (ionization) energies (24), following the pioneering work of

Pearson & Bardeen (25). These differed for different donors and acceptors, showing for the first time the importance of local field effects, although the binding energies were roughly in agreement with a hydrogen-like model having greatly enlarged orbits due to the large dielectric constant of the host semiconductor. The many infrared investigations that followed revealed their excited state energies. Later the exquisite ENDOR (electron nuclear double resonance) experiments mapped out the trajectory of the enlarged wave function (26).

Having spent laborious hours calibrating secondary thermometers during my thesis work, I had the satisfaction, following earlier work (27), of finding that properly doped germanium can make a reliable secondary thermometer that is highly reproducible upon temperature cycling (28), a major improvement over previously used bronze and carbon thermometers (see, for example, Reference 29).

Superconductors

My fascination with superconductivity began in graduate school. In my qualifying exam, I reviewed Daunt and Mendelssohn's experiment, which showed that the Thomson coefficient in a thermoelectric superconducting circuit is zero, meaning the supercurrents carry no entropy (30). Partly from this experience, when Bernd Matthias proposed that I join in the hunt for new superconductors, I readily accepted.

Hardy and Hulm's discovery of superconductivity in V_3Si with the cubic A15 structure and the remarkably high $T_c \sim 17$ K led Bernd to synthesize other A15 compounds including the previously unknown compound Nb_3Sn. It formed with its stoichiometric 3:1 composition simply by reacting Nb powder with molten Sn, and we found it to have a record high T_c of just over 18 K. The solid state community at that time was concerned with Fermiology and with superconductivity in pure metals and dilute alloys. A15 superconductivity was more or less ignored as being more alchemy than solid state physics. The pioneering work of Meissner who first discovered strange superconductors, such as CuS, has also been ignored and for a much longer time. In my opinion, Meissner deserves as much recognition for that work as for the famous Meissner-Oschenfeld effect.

The discovery of the BCS (Bardeen-Cooper-Schrieffer) microscopic theory of superconductivity two years later did nothing to change the attitude that superconductivity of complex compounds was too messy to warrant serious study. Ultimately, the impetus for further investigating Nb_3Sn came from technology—the need to shield the three-level microwave amplifiers (masers) that were being designed for the next-generation communication network led Rudi Kompfner, a director in the Communications Department, to suggest using Nb_3Sn (R.J. Kompfner, personal communication). In response to that need, Kunzler et al. (31) discovered the high-field, high-current capabilities of Nb_3Sn. These valuable properties have led to the construction of magnets needed for MRI imaging, high-energy physics accelerators, electrical power technologies, and hopefully the confinement of the hot (~100,000,000-K) plasma to be produced in the experimental international thermonuclear fusion reactor (ITER) within the next decade. The misguided sponge theory was replaced by Abrikosov's theory, and type II superconductivity became a frontier field in condensed matter physics. Later on at Stanford when it became possible to grow thin films of metastable A15 compounds, we were able to find out much more about the physics of A15 superconductivity (see below). My experience with Nb_3Sn has remained a central influence on my career throughout the years. I firmly believe that novel behavior even from ill-characterized samples should be investigated at least far enough to assure that the baby is not thrown out with the bath water.

By simply averaging over the periodic table using a rigid band approach, Matthias had by this time discovered many new superconductors. This experience led to his formulation of the Matthias

rules, which predicted the occurrence of superconductivity based simply on the number of valence electrons per atom, i.e., based simply on the average filling of the transition-metal d-bands (32). The exceptions to his rules proved most interesting to me, because they signaled the possibility of new physics or unexpected materials science. Here are some examples:

1. The increase in the T_c of Ti upon addition of small concentrations of Fe is an order of magnitude greater than expected from the Matthias rules, whereas the rules do hold for the other transition-metal elements. Could this be due to some new pairing mechanism associated with Fe? Raub et al. (33), employing classical metallurgy, found otherwise. The apparently anomalous behavior was due to the filaments of bcc Ti that were inhomogeneously distributed in the majority hcp phase. The bcc Fe was preferentially concentrated in those filaments with a value consistent with the Matthias rules.

2. In a related case, filaments of superconducting $LaRh_5$ were found to precipitate from a $La_{.01}Rh_{.99}$ melt and to form a scaffold with connected $LaRh_5$ filaments that give complete shielding (34) and sharp transitions when warmed in a magnetic field that is applied after cooling in zero field. (This procedure has become known as zero-field cooling. It is valuable for detecting superconductivity but can easily overestimate the superconducting volume fraction.) However, a 0.1% solution ($La_{.001}Rh_{.999}$) gave broad zero-field cooled signals. Transition electron microscopic images showed that in this latter case, the superconducting filaments of $LaRh_5$ were disconnected, thus providing early support for proximity effect coupling. The addition of a small concentration of Fe to the 1% and 0.1% samples gave convincing support. No effect on T_c was observed for the 1% sample, whereas T_c was no longer observed in the 0.1% sample. Fe is nonmagnetic in $LaRh_5$ and is a magnetic pair breaker in Rh. The temperature and field-sensitive bronze thermometers used for so many years at Leiden as mentioned above must have been due to proximity-connected Pb filaments, although to my knowledge the underlying physics remained a mystery.

In searching for new pairing mechanisms beyond phonon-mediated ones, we noticed that the $M^{-1/2}$ mass dependence of T_c, known as the isotope effect, the sine-qua-non of BCS superconductivity at that time, had been tested with non-transition metals only (35). We decided it would be fruitful to extend the isotope-dependent investigations to transition metals with the thought that their more localized d-bands might give rise to a nonphonon mechanism of pairing. The first transition metal measured, Ru ($T_c \sim 0.5$ K), exhibited a nondetectable dependence of T_c on mass (36), and for a short time I believed we had made a major discovery. However, a few doors down the hall from my lab, Phil Anderson and his student Pierre Morel (37) were using Eliashberg theory to find that the mass dependence of the renormalized Coulomb interaction μ^* that is of the opposite sign and of sufficient magnitude to roughly cancel the pre-exponential energy factor ω_0 in the BCS expression for T_c was responsible for the $M^{-1/2}$ dependence found in non-transition-metal elements (35). Their analysis provided me with a rationale for understanding why Nb-containing compounds always have higher T_c's than comparable compounds containing other transition elements. The retarded interaction is localized in space so the observation can be understood if local correlations around Nb are more favorable.

The lack of superconductivity in pure Mo, which had been found to be nonsuperconducting down to 0.01 K, was at odds with BCS predictions. Once again, the seemingly unusual behavior had a straightforward materials science explanation. We found that previous investigators must have used Mo that contained traces of Fe. When Ernie Corenzwit prepared the Mo sample by arc-melting a high-purity commercial sample, Fe was removed, simply by evaporating, and we found Mo to be superconducting with a T_c of ~1 K. The Fe is a pair breaker that reduces T_c at a record rate of ~100 K per percent Fe (38). Fe present in one part in 10,000 is thus sufficient to account for the

lack of superconductivity found in the previous work. The intermediate isotope effect we found for Mo was, moreover, quite reasonable (39).

The unexpected discovery of superconductivity in a sample from another department investigating low work functions led to our discovery of graphite intercalated with alkali metals (40) and was my first encounter with the fascinating properties of layered structures, which I continued to pursue later at Stanford, and which has become a major theme in condensed matter physics. And there still may be more discoveries to come. Hysteresis loops that have been measured in graphite samples at temperatures as high as room temperature remain to be tracked down (41). Wanting to find out why is an example of my unfashionable interest in unidentified superconducting objects (USOs). USOs describe anomalies that might be due to the presence of a small amount of a novel high-superconducting phase embedded in the parent material, but are more often due to spurious nonsuperconducting inhomogeneities and less interesting materials science—but who can know when a USO will prove to be the real thing?

Ternary Transition-Metal Oxides

Ternary transition-metal oxides have a rich variety of magnetic and superconducting properties. The pioneering investigations at the Philips Eindhoven Laboratory showed that simple ionic substitutions in $LaMnO_3$ can be used to control magnetic and resistive properties and understood by ionic chemistry and the mechanism of double exchange (42). We became directly interested in this material following the discovery of giant magnetoresistance, as is discussed below. But from the perspective of superconductivity, what is of interest here is the discovery of superconductivity in $SrTiO_3$ by Marvin Cohen and coworkers at the Naval Research Lab (43), which opened the door to a new class of ternary oxide superconductors. The related alkali metal tungsten bronzes were soon found to be superconducting (44). We later found that the T_c of related K_xWO_3 increases when the stoichiometric concentration $x = 1/3$ is decreased by etching away the K and continues to do so until the bulk crystal is no longer stable (45). It is intriguing to ask whether the unconfirmed T_c's ~90 K later reported in Na_xWO_3 crystals (46) are a continuation of the same trend of increasing T_c's with decreasing carrier concentration. Regions with much lower carrier concentration are possibly stabilized by the graded epitaxy that naturally occurs when Na is evaporated from the surface of the perovskite crystal. However, the signal around 90 K could be due to an unidentified reconstruction near the surface. Art Sleight and coworkers discovered superconductivity with surprisingly high T_c's (a T_{cmax} of ~13 K) in $BaBiO_3$, a charge density wave insulator, which becomes a superconductor when doped on the Bi site with Pb (47); later, Mattheiss and coworkers discovered even higher T_c's up to ~ 30 K when $BaBiO_3$ is doped with K on the Ba site (48). Many theories have been proposed to explain the pairing mechanism. The chemically intuitive approach that appeals to me favors the local configuration of Bi, which makes it tend to be a valence-skipping element, a chemical property that is well known in many solid state contexts (49). Indeed, there is some intriguing circumstantial evidence that pairing persists in the normal state (above T_c) in these materials and that the transport is by charge 2e bosons (50). As in the case of the WO_3 bronzes discussed above, the pairing in $BaBiO_3$ weakens with doping as the conductivity increases, suggesting that T_c is maximized by an optimum amount of screening. The idea that a largely electronic attraction between two electrons can occur in certain local environments is referred to as negative-U centers and is not a new idea, but negative-U *pairing* centers are special and are another obsession to which I have returned many times.

STANFORD

Solid state physics emerged from its quantum mechanical purity (i.e., free electron gas and tight-binding models) to become a serious study of real materials in the 1940s (51), and it provided the

basis for the invention of the transistor and the semiconductor technology we know today. The introduction of condensed matter physics at Stanford must not be untypical of how it grew in other research universities. Gerald Pearson left Bell in 1960 to become a professor in electrical engineering and initiate semiconductor research at Stanford. Shortly thereafter, the Physics Department cautiously authorized one single appointment in solid state physics. Marvin Chodorow, who conducted the search, was unable to decide between two desirable scientists. The provost created the Division of Applied Physics and Science to accommodate both. Arthur Schawlow was appointed to Physics and Calvin Quate to the new Division. The Division proved to be attractive to students and soon became a graduate department in the School of Humanities and Sciences. Walter Harrison joined the Division in 1965, and Arthur Bienenstock and I received joint appointments in that division and in the Materials Science and Engineering Department in 1967. I continued for some time to be a part-time staff member at Bell as well.

I have often been asked what the difference is between the Applied Physics and the Physics departments. The two departments have many common intellectual interests including superconductivity. The distinction is that Applied Physics is also engaged in possible technological applications,[3] whereas Physics is also engaged in string theory. This is a good place for me to acknowledge the sustained support I have received since being at Stanford from the Air Force Office of Scientific Research. It has held steadfastly to the belief that fundamental condensed matter research can in the long run lead to the discovery of new superconductors, which in turn can lead to components that improve airplane performance.

I soon found that one of the most rewarding parts of doing research at a university is the students. They come fresh, enthusiastic, open to new ideas, and believing that textbooks and professors know it all. Then they start thinking for themselves and I start learning from them. There isn't room here to do more than express the enjoyment I have in following the careers my students are having, some in academia, others in industrial and national labs in the United States and elsewhere.[4]

When I first arrived at Stanford, I recruited Rick Greene, a fresh PhD from Art Schawlow's group, and other talented students to transform an empty room into a new laboratory where we continued the search for superconductors and materials that didn't seem to play by the normal rules of solid state physics. We were soon rewarded when Dick Klemm, an undergraduate, reported on a new reaction in which organic molecules can be intercalated into transition-metal dichalcogenides (52). This led to the discovery of dozens of new superconductors in which the spacing between the 2D conductors and the T_c's depended upon the length and packing density of the intercalated species (53) (**Figure 1**).

The Lawrence-Doniach model of 2D Josephson tunneling (54) shows why T_c could be independent of the spacing. A nice experimental demonstration is shown in **Figure 1**. The intriguing increase in T_c upon the intercalating TaS_2 with ammonia that I had hoped might be the signal of an additional pairing mechanism was later shown to be due to the destruction of a competing charge density wave (55, 56, 127). Incommensurate charge density wave transitions were discovered for the first time in the course of related studies by Wilson et al. (56).

Mac Beasley came to Stanford in 1973. We built a research group that appealed to students who liked bench-top experiments where they could be engaged in all aspects of the research from synthesis, to measurement, to interpretation, and with plenty of opportunity for self-feedback. New synthesis methods are often the harbingers of new avenues for physics

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[3]The formation of Conductus, a start-up company, is an example discussed below.

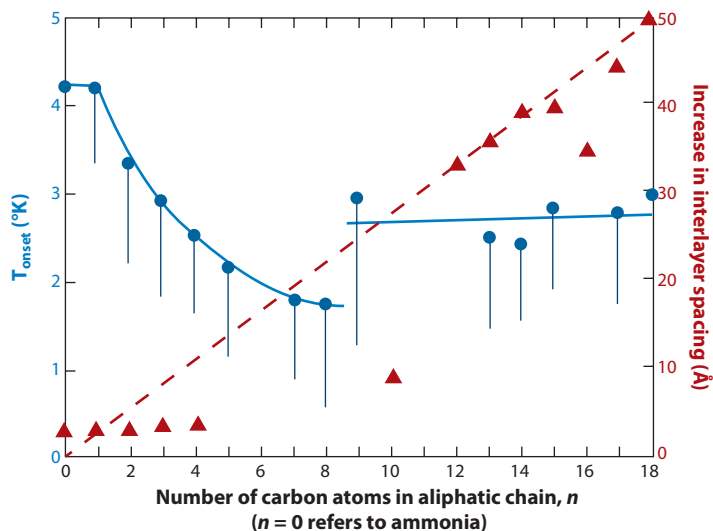[4]The first child of my last student, Daniel Worledge, is named Theodora.

Figure 1

The interlayer spacing (*red*) and T_c (*blue*) as a function of the length of the intercalated aliphatic amines CH3-(CH2)$_{(n-1)}$-NH2. Up to $n = 8$, the interlayer spacing stays constant, indicating that the amines lie flat with the result that the density of N-S bonds and T_c decrease. For $n > 8$, the spacing between the layers increases linearly with n indicating that the amines are aligned perpendicular to the layers, and the density of N-S bonds and T_c remain constant (127). For T_c, the circles represent the onsets of the transitions, and the vertical lines represent their widths as determined by low-frequency magnetic susceptibility measurements.

discovery. For our group at Sanford, thin-film synthesis gave us the chance to explore properties of correlated electron fluids. Our group, along with many other research groups, profited from the advances in thin-film deposition and characterization techniques that rapidly evolved in semiconductor technology. We eventually employed four versatile deposition systems for extending phase diagrams for obtaining metastable and amorphous phases and for depositing multilayered heterostructures, interfaces, and tunnel junctions as discussed below.

1. The e-beam system designed by Bob Hammond deposits flux generated from linear arrays of electron beam–heated sources with rapid feedback control and in situ diagnostics. It was originally used in a project with Cal Quate, Andy Phillips, Mac Beasley, Bob Hammond, and myself and students to investigate the use of Nb$_3$Sn in superconducting power transmission lines (57), and later for pioneering epitaxial growths to obtain metastable films of A15 superconductors and amorphous transition-metal junctions (58, 59, 60) and for preparing samples of superconducting cuprates. The ion-beam-assisted-deposition (IBAD) procedure developed at the IBM laboratories by Jim Harper, one of our graduate students (61), was incorporated in the system (62). The focused ion beam removes all orientations of the growing film that are initially deposited, except the one that is transparent to the focused beam, thus leaving a thin highly oriented template suitable for homoepitaxial growth. It proved to be valuable for eliminating grain boundaries and leaving a highly oriented surface suitable for homoepitaxial growth. Further work shows it has potential for producing long lengths of superconducting wire (63).

2. The planar magnetron sputtering system developed by Doug Keith and Troy Barbee at the Stanford Center for Materials Research made it possible to investigate amorphous

Mo_xGe_{1-x} films over a wide range of composition encompassing the insulator/metal (64) and superconducting transitions (65, 66). It made possible investigations into the superconducting properties of fine-scaled transition-metal multilayered films (67, 68). The 90° off-axis configuration produced excellent films because it minimized or eliminated secondary sputtering of oxygen in the film by high-speed particles in the flux (69).

3. The pulsed laser deposition (PLD) has become a favored method (70). It has mostly displaced magnetron sputtering for a number of reasons. Reliable excimer laser systems that have become commercially available provide excellent control of the deposition parameters. The ablation process itself preserves the composition of the target. Smooth TiO_2-terminated surfaces on $SrTiO_3$ substrates can be easily prepared using the method of Koster et al. (71) that, with in situ control with reflection high-energy electron diffraction (RHEED) control, makes possible epitaxial growth with layer-by-layer control. Ohtomo & Hwang's (72) discovery of superconductivity at the interface between two insulating oxides, $SrTiO_3$ and $LaAlO_3$, deposited from PLD targets has created a new frontier in interface research. Furthermore, buffer layers allow for the epitaxial growth of cuprates on silicon substrates (73) and other 3–5 semiconductors.

4. The sophisticated molecular beam epitaxy techniques used in semiconductor research were successfully adapted by a Varian-Stanford collaboration (74) [and further refined by Eckstein et al. (75)] for the growth of oxides by incorporating an ozone source into the high vacuum system. Multiple sources with computer-controlled shutters make it possible to deposit sharp interfaces. It has been shown that at an interface between antiferromagnetic and superconducting phases occurs over distances of less than one unit cell (76)! Remarkably Bozovic et al. (77) have demonstrated that the superconductivity originating near an interface between nonsuperconducting underdoped and overdoped cuprates occurs in the second, and only in the second, CuO_2 layer from the interface, a finding that cannot be accounted for by ionic diffusion.

When John Rowell visited Stanford on a sabbatical in 1974–1975, he added to our know-how for making tunnel junctions and for using the McMillan-Rowell program for making spectroscopic investigations of $\alpha^2F(\omega)$ of the A15 superconductors (78–80). We were able to complement our investigations of their strong-coupling properties that were obtained by developing silicon-on-sapphire calorimeters capable of measuring heat capacities of films containing as little as 1 mg of material (81, 82). As the stoichiometric composition is approached in Nb_3Sn (83), Nb_3Al (79), and Nb_3Ge (80), the phonons soften, and the BCS fitting parameters reach strong-coupling values. A quasi one–dimensional model has been proposed to account for the data by Labbe & Friedel (84) and by Weger & Goldberg (85). The one-dimensionality is attributed to linear arrays of closely spaced, nonintersecting Nb or V ions aligned in the three cubic directions. The low T_c's that are found in all Nb-rich compositions can be understood because the one-dimensionality is destroyed by the excess niobium atoms connecting the chains. Admittedly, as far as I know, no quasi one–dimensional features have appeared in band structure calculations, which has led many theorists to discount quasi-one dimensionality. However, I trust the intuitive approach (although I get flack for this from some colleagues). A15 superconductivity has not been at the forefront of condensed matter physics since 1987, but I believe now is a time to revisit with the benefit of all that has been learned since the discovery of the cuprates.

One of the more tantalizing compounds we investigated was CuCl. A visitor of Walt Harrison's from Russia, Sasha Russakov, came with some novel ideas about the behavior of the band structure under pressure and the possibility of superconductivity. We investigated this

possibility with Paul Chu, who contributed his high-pressure expertise. We observed transient inductive and resistive superconducting–like signals in a narrow range of temperatures around 185 K when the CuCl samples were warmed under pressure (86–88). Because these transient signals were reproduced from run to run, I believe they could be due to a metastable superconducting phase or interface resulting from the disproportionation reaction $Cu^{+1} = Cu + Cu^{+2}$. More recently, CuO/Cu interfaces heated and quenched by short high-current pulses have been reported to give indications of superconductivity at very high temperatures (89).

CuO itself, unlike other 3D transition-metal oxides that have rock salt structures, is monoclinic due to a strong Jahn-Teller distortion. Thin films have been epitaxially stabilized in a tetragonal phase by Siemons et al. (90); however, doping experiments so far have been unsuccessful in obtaining metallic conductivity. CuO/Cu interfaces have been investigated by Munakata et al. (91), who show evidence for a new type of proximity-induced antiferromagnetism in the copper. However, no indication of superconductivity has been found in equilibrium interfaces. If superconductivity does exist, it will probably be in metastable interfaces far from equilibrium.

Post-Cuprate Era

Aharon Kapitulnik came to Stanford in 1985 with plenty of new ideas. He immediately helped in understanding the semiconductor-to-superconducting transition that occurs when La is added to the La vacancies in the La_2S_3 unit cell. This is a nice system because the transition occurs while the sulfur framework remains unchanged (92).

By 1986, my belief was that superconductivity, with the exception of some unresolved USOs, was well understood. With mandatory retirement looming (at that time I was 70), I started thinking about growing artichokes in Pescadero, CA. Then, a short paper, "Possible High T_c Superconductivity in the Ba-La-Cu-O System," by Bednorz & Müller (93) in the IBM Zurich Research Laboratory, reported a broad resistive transition when a T_c of ~30 K appeared. A possible USO-type explanation was dispelled when the result was immediately verified in Japan (94) and soon duplicated everywhere. The further discovery of T_c's above liquid nitrogen temperatures by Chu, Wu, and coworkers (95) gave rise to unprecedented excitement, which reached a peak in the "Woodstock of Physics" APS meeting. At Stanford we, along with many others, were early contributors to the onslaught of HiT$_c$ research that followed.[5] We were soon able to capitalize on our experience with epitxial growth and used $SrTiO_3$ substrates to obtain films in different orientations, and with graded compositions (96, 97).

Although there is overwhelming experimental and theoretical evidence that superconductivity originates in the CuO_2 layers, there is also some experimental evidence that suggests pairing interactions occur elsewhere in the unit cell. One example is in the 248 double chain–layered superconductors: NMR results reveal superfluid density in the double chains (98). This and other evidence cannot be explained as being proximity-induced from the CuO_2 layers. Moreover, it has

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[5]The unbounded potential for superconducting technologies operating at liquid nitrogen temperatures was very soon appreciated by venture capitalists. A group of us—Mac Beasley, Aharon Kapitulnik, Bob Hammond, and me from Stanford and John Clarke, Paul Richards, and Ted Van Duzer from Berkeley— were offered start-up funds to organize a company, Conductus, with no business plan other than to explore opportunities. After some time, John Rowell joined as the Chief Technical Officer and brought along Bob Dynes. The freewheeling atmosphere and a talented staff led to outstanding technical achievements. Unfortunately, the main product, a superconducting front-end receiver for wireless base stations, which offered enhanced coverage and increased sensitivity (hence fewer dropped calls), did not develop the hoped-for market. I believe having to operate at liquid nitrogen temperatures presented too high a barrier. Conductus' method for producing tape is still being improved and may still play an important role in future superconducting transmission lines.

been shown theoretically that superconductivity can originate from interactions within double chains (99).

To explain why T_c roughly doubled when charge reservoir layers (HgO_x, TlO_x, or BiO) were inserted between the SrO layers in optimally doped 214 $(LaSr)_2CuO_4$, we suggested there might be a second pairing mechanism due to enhancement by negative-U pairing centers in the charge reservoir layer (100). In contrast, a recent theory asserts that T_c, rather than being enhanced by interactions in the charge reservoir layer, is depressed in optimally doped 214 because the shorter apical oxygen distance increases orbital overlap of the apical oxygen with near-neighbor Cu ions in the CuO_2 layer and depresses T_c. I believe that theory is incomplete because under hydrostatic pressure, the apical oxygen distance is reduced so that it becomes comparable to the distance in optimally doped 214 material, whereas the CuO bond distance remains much larger and, contrary to the theoretical predictions, T_c increases rather than decreases. Further theoretical and experimental investigations are needed, and I have hopes they will lead to even higher T_c's. (I have enjoyed discussions with Doug Scalapino, Sri Raghu, and Steve Kivelson on this complex problem.)

Chen and coworkers' (101) discovery of colossal magnetoresistance behavior in the manganate perovskite family, three orders of magnitude greater than previously known, led us to investigate $La_{.67}Ca_{.33}MnO_3$ (102). $La_{.67}Ca_{.33}MnO_3/SrTiO_3/Al$ tunnel junctions (103) were prepared following the pioneering work of Meservey & Tedrow (104), and large spin-polarized currents were found. This led to Worledge's proposal of a new concept, the double spin-filter tunnel junction, in which the magnetic elements are the barrier rather than the electrodes (105). The resistance is low when the moments are parallel and high when they are antiparallel. Calculations show that it can have orders of magnitude greater sensitivity than previous tunnel junction configurations. Experimental investigations of this promising model are underway (106).

In 2000, Ian Fisher came to Stanford. His expertise in single-crystal growth added a whole new dimension to our synthesis capabilities. Following earlier work in Russia (107), we confirmed that Tl becomes a localized negative-U (108) pairing center[6] when substituted for divalent Pb in semiconducting PbTe (109). In ionic crystals, Tl is known to avoid being in a $6S^1$ configuration and disproportionates into configurations with filled and unfilled 6S shells: $2Tl^{+2} \Rightarrow Tl^{+1} + Tl^{+3}$. At the lowest concentration of Tl that induces superconductivity in PbTe, $\sim0.3\%$, Hall measurements show that the +1 and +3 states become degenerate in energy, and, significantly, the resistance data show that a charge Kondo two-level state is formed (110). This requires the exchange of pairs of electrons between virtual negative-U-bound pairs and the valence band. Recent theoretical models can account for the unusual relationships and show that there is an intimate connection between the charge Kondo problem and the negative-U superconductivity (111, 112).

The above research attempted to find a model system that would lend credibility to the possibility that local correlations would cause Tl, Hg, or Bi ions in the charge reservoir theses ions to form virtual two-electron-bound states and become pairing centers responsible for the enhancement of T_c discussed above. The in situ photoemission studies by Terada et al. (113) showed the Tl 4f peak to be intermediate between Tl +1 and +3, and I took this (incorrectly) to be "smoking gun" evidence for the pairing mechanism. But one would expect the strength of the pairing would be different for Tl and Hg ions. However, experiments by Iyo et al. (114) find almost identical T_c's for $n = 3$ to 5 CuO_2 layers of Hg and Tl cuprates. It would be an unlikely

[6]Negative-U pairing is not a new idea—it is well known to occur in chalcogenide glasses where the Coulomb repulsion is overcompensated by the lattice response, which leads to self-trapped bipolarons or as well known in chemical terms as electron pairs (108).

coincidence for two different negative-U centers to be of equal strength. A more likely model that depends on the screening of the long-range repulsive Coulomb interactions in the charge reservoir layers is promising (115). It suggests the possibility of increasing T_c in the 214 cuprates by adding other screening layers.

I haven't given up on the idea that there are as yet undiscovered pairing mechanisms in the cuprates. There are two families of cuprates that have high T_c's ($\sim$90 K) and yet show evidence for the valence of copper being well beyond 2.3 where only Fermi liquid metals are believed to exist. Unfortunately, they are metastable and must be synthesized under high pressures and temperatures in strongly oxidizing conditions. Massimo Marezio and I have analyzed existing data obtained in metastable 214 $Sr_2CuO_{(4-v)}$ samples by a number of groups two decades ago (116–119), and more recently by Liu et al. (120), and find reasonable evidence that the superconductivity exists in very overdoped samples (121). The location of the vacancies, v, is controversial because the samples are not single phase, but the magnitude of the Meissner signal is large enough to preclude the signals coming from a minority phase.

A second cuprate family with a high Cu valence and high T_c's is found in single-phase samples for which neutron diffraction data have been refined (122). The first member of the family has the same structure as the familiar Y123 structure but with one-quarter of the Cu chain ions replaced by Mo. Its formula is abbreviated as $(Cu_{.75}Mo_{.25})-12s2$. For $s = 1$, $T_c = 87$ K, and the Cu valence in the CuO_2 layers is 2.5, as determined by the empirical bond valence sums based on neutron diffraction, and by XANES (X-ray absorption near edge structure). It remains to be established as to whether this high valence indicates that all the electrons removed from the Cu have doped the CuO_2 valence band, although it seems likely to me and suggests there may be a second "dome" in the doping profiles beyond the levels in which other cuprates are Fermi liquids. The higher members of the family contain additional insulating $(CeY-O_2-CeY)_{s-1}$ fluorite layers between the two CuO_2 layers that block interlayer tunneling; T_c drops to a constant 57 K for $s = 2$ to 4; and the Cu valence determined as above is 2.3, a valence at which other cuprates are found to be normal Fermi liquids. Again, more experimental investigations are needed.

FUTURE

The unexpected discovery of superconductivity in the interface between insulating $SrTiO_3$ and insulating $LaAlO_3$ (72) has been followed by many other studies of superconductivity and other ordering phenomena at interfaces (123), suggesting that maybe just the tip of the iceberg has been observed. Many more metastable phases and interfaces remain to be investigated; more novel phenomena are bound to be found. The proposal by Berg et al. (124) is a good challenge for experimentalists. They studied an interface where one side has a large pairing energy, Δ, but has zero superfluid density or T_c, and the other is a normal metal. If the chemical potentials can be adjusted to allow coherent tunneling, their analysis shows that the T_c of the composite can be as high as $\Delta/2$. If the tunneling is by 2e bosons, as might be the case for $BaBiO_3$ (125), the physics could be related to that described above for (PbTl)Te.

A few intriguing USOs, such as metastable CuCl and CuO, remain challenging. I have discussed in more detail the reasons for believing there might be pairing mechanisms other than the presently accepted ones in the special volume of the *Journal of Superconductivity and Novel Magnetism* (126) dedicated to Vitaly Ginzburg on his 90th birthday. I am optimistic that the time is ripe for some new Matthias-Hulm, Bednorz-Müller, or Chu-Wu combination to come forth and lead us from the cold cryogenic country into fertile fields of room-temperature superconductivity. I can see that Promised Land ahead, although I may not live long enough to get there.

DISCLOSURE STATEMENT

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LITERATURE CITED

1. Moyzhes BY, Geballe TH. 2005. The thermionic energy converter as a topping cycle —new triode designs with a longitudinal magnetic field. *J. Phys D. Appl. Phys.* 38:782–86
2. Leighton RB. 1948. The vibrational spectrum and specific heat of a face-centered cubic crystal. *Rev. Mod. Phys.* 20:165–74
3. Giauque WF. 1969. Notes on assembly and experimental procedure with low-temperature calorimeters, the calculation of heat capacity, and the resistance-temperature calibration of a resistance thermometer. In *The Scientific Papers of W F Giauque*, Vol 1, Giaque Sci. Pap. Found., Pap. 38, pp. 332–68. New York: Dover Publ. Inc.
4. Geballe TH, Giauque WF. 1952. The heat capacity and entropy of gold from 15 to 300 degree K. *J. Am. Chem. Soc.* 74:2368–72
5. Giauque WF, MacDougall DP. 1933. Attainment of temperatures below 1° absolute by demagnetization of Gd2(SO4)3·8H2O. *Phys. Rev.* 43:768
6. Beevers CA, Lipson H. 1934. Crystal structure of CuSO4· 5H2O. *Proc. R. Soc. London* 146:570–82
7. Krishnan KS, Mookherji A. 1938. The magnetic anisotropy of copper sulphate pentahydrate, $CuSO_4 \cdot 5H_2O$, in relation to its crystal structure. Part II. *Phys. Rev.* 54:533–39
8. Giauque WF, Geballe TH, Lyon DN, Fritz JJ. 1952. Some properties of plastics and the use of plastic apparatus at low temperatures *Rev. Sci. Instrum.* 23:169–73
9. Geballe TH, Giauque WF. 1952. The heat capacity and magnetic properties of single crystal copper sulfate pentahyrdrate from 0.25 to 4°K.[1] *J. Am. Chem. Soc.* 74:3513–19
10. Anderson RJ, Giauque WF. 1967. Heat capacity, entropy, and magnetic moment of single-crystal $CuSO_4 \cdot 5H_2O$ with fields to 90 kG II to the α magnetic axis. *J. Chem. Phys.* 46:2413–28
11. White RM, Geballe TH. 1979. *Long Range Order in Solids*, Solid State Series, ed. E Seitz, D Turnbull. New York/London: Academic
12. Geballe TH, Hull GW. 1954. Seebeck effect in germanium. *Phys. Rev.* 94:1134–40
13. Gurevich L. 1945. *J. Phys. (U.S.S.R.)* 9:477
14. Frederikse HPR. 1953. Thermoelectric power of germanium below room temperature. *Phys. Rev.* 92:248–52

15. Herring C. 1954. Theory of the thermoelectric power of semiconductors. *Phys. Rev.* 96:1163–87

16. Geballe TH, Hull GW. 1955. Seebeck effect in silicon. *Phys. Rev.* 98:940–47

17. Herring C, Geballe TH, Kunzler JE. 1959. Analysis of phonon-drag thermomagnetic effects in n-type germanium. *Bell Syst. Tech. J.* 38:657–747

18. Pomeranchuk I. 1942. About thermal conductivity of dielectrics. *J. Phys. (USSR)* 6:237–46

19. Geballe TH, Hull GW. 1958. Isotopic and other types of thermal resistance in germanium. *Phys. Rev.* 110:773–75

20. Slack GA. 1957. Effect of isotopes on low-temperature thermal conductivity. *Phys. Rev.* 105:829–31

21. Anthony TR, Banholzer WF, Fleischer JF, Wei L, Kuo PK, et al. 1990. Thermal diffusivity of isotopically enriched sup 12/C diamond. *Phys. Rev. B* 42:1104–11

22. Hubbard J. 1963. Electron correlations in narrow energy bands. *Proc. R. Soc. Lond. A* 276:238–57

23. Pollak M, Geballe TH. 1961. Low-frequency conductivity due to hopping processes in silicon. *Phys. Rev.* 122:1742–53

24. Geballe TH, Morin FJ. 1954. Ionization energies of groups III and V elements in germanium. *Phys. Rev.* 95:1085–86

25. Pearson GL, Bardeen J. 1949. Electrical properties of pure silicon and silicon alloys containing boron and phosphorus. *Phys. Rev.* 75:865–83

26. Feher G. 1959. Electron spin resonance experiments on donors in silicon. I. Electronic structure of donors by the electron nuclear double resonance technique. *Phys. Rev.* 114:1219–44

27. Friedberg S. 1951. *Phys. Rev.* 82:764

28. Geballe TH, Morin FJ, Maita JP. 1955. *Some low-temperature thermometric properties of germanium.* Presented at Conference de Physique des Basses Temperatures, Paris; Kunzler JE, Geballe TH, Hull GW. 1957. Germanium resistance thermometers suitable for low-temperature calorimetry. *Rev. Sci. Instr.* 28:96–98

29. Keesom PH, Pearlman N. 1956. *Handbuch der Physik Vol. XIV*, ed. S Flügge. Berlin: Springer-Verlag

30. Daunt JG, Mendelssohn K, 1946. An experiment on the mechanism of superconductivity. *Proc. R. Soc. Lond. A* 185:225–39

31. Kunzler JE, Buehler E, Hsu FSL, Wernick JH. 1961. Superconductivity in Nb$_3$Sn at high current density in a magnetic field of 88 kgauss. *Phys. Rev. Lett.* 6:89–91

32. Matthias BT. 1955. Empirical relation between superconductivity and the number of valence electrons per atom *Phys. Rev.* 97:74–76

33. Raub E, Raub CJ, Röschel E, Compton VB, Geballe TH, Matthias BT. 1967. The α-Ti-Fe solid solution and its superconducting properties. *J. Less-Common Met.* 12:36–40

34. Arrhenius G, Fitzgerald R, Hamilton DC, Holm BA, Matthias BT, et al. 1964. Superconducting tubes and filaments. *J. Appl. Phys.* 35:3487–91

35. Maxwell E. 1950. Isotope effect in the superconductivity of mercury. *Phys. Rev.* 78:477; Reynolds CA, Serin B, Wright WH, Nesbitt LB. 1950. Superconductivity of isotopes of mercury. *Phys. Rev.* 78:487

36. Geballe TH, Matthias BT, Hull GW Jr, Corenzwit E. 1961. Absence of an isotope effect in superconducting ruthenium. *Phys. Rev. Lett.* 6:275–77

37. Morel P, Anderson PW. 1962. Calculation of the superconducting state parameters with retarded electron-phonon interaction. *Phys. Rev.* 125:1263–71

38. Geballe TH, Matthias BT, Corenzwit E, Hull GW Jr. 1962. Superconductivity in molybdenum. *Phys. Rev. Lett.* 8:313

39. Geballe TH, Matthias BT. 1962. Isotope effects in low temperature superconductors. *IBM J. Res. Develop.* 6:256–57

40. Hannay NB, Geballe TH, Matthias BT, Andres K, Schmidt P, MacNair D. 1965. Superconductivity in graphitic compounds. *Phys. Rev. Lett.* 14:225–26

41. Kopelevich Y, da Silva RR, Torres JHS, Moehlecke S, Maple MB. 2004. High-temperature local superconductivity in graphite and graphite-sulfur composites. *Phys. C* 408:77–78

42. Jonker GH, Van Santen JH. 1950. Ferromagnetic compounds of manganese with perovskite structure. *Physica* 16(3):599–600; Jonker GH, Van Santen JH. 1950. Electrical conductivity of ferromagnetic compounds of manganese with perovskite structure. *Physica* 16:599–600; Snyder GJ,

Hiskes R, DiCarolis S, Beasley MR, Geballe TH. 1996. Intrinsic electrical transport and magnetic properties of La0.67Ca0.33MnO3 and La0.67Sr0.33MnO3 MOCVD thin films and bulk material. *Phys. Rev. B* 53:14434–44

43. Schooley JF, Hosler WR, Cohen ML. 1964. Superconductivity in semiconducting SrTiO3. *Phys. Rev. Lett.* 12:474–75

44. Raub ChJ, Sweedler AR, Jensen MA, Broadston S, Matthias BT.1964. Superconductivity of sodium tungsten bronzes. *Phys. Rev. Lett.* 13:746–47

45. Remeika JP, Geballe TG, Matthias BT, Cooper AS, Hull GW, Kelly EM. 1967. Superconductivity in hexagonal tungsten bronzes. *Phys. Lett. A* 24:565–66

46. Reich S, Tsabba Y. 1999. Possible nucleation of a 2D superconducting phase on WO3 single crystals surface doped with Na+. *Eur. Phys. J. B* 9:1–4; Reich S, Leitus G, Popovitz-Biro R, Goldbourt A, Vega S. 2009. A possible 2D HxWO3 superconductor with a *Tc* of 120 K. *J. Supercond. Novel Magnet.* 22:343–46

47. Sleight AW, Gillson JL, Bierstedt PE. 1975. High-temperature superconductivity in the BaPb1-xBixO3 systems. *Solid State Commun.* 17:27–28

48. Mattheiss LF, Gyorgy EM, Johnson DW Jr. 1988. Superconductivity above 20 K in the Ba-K-Bi-O system. *Phys. Rev. B* 37:3745–46

49. Varma CM. 1988. Missing valence states, diamagnetic insulators, and superconductors. *Phys. Rev. Lett.* 61:2713–16

50. Taraphder A, Pandit R, Krishnamurthy HR, Ramakrishnan TV. 1996. The exotic barium bismuthates. *Int. J. Mod. Phys. B* 10:863–955

51. Seitz F. 1941. *The modern theory of solids.* New York: McGraw Hill

52. Weiss A, Ruthardt R. 1969. Schichteinlagerungs-Verbindungen des Titandisulfids mit Säureamiden. *Z. Naturforschung Teil B* 24:355

53. Gamble FR, DiSalvo FJ, Klemm RA, Geballe TH. 1970. Superconductivity in layered structure organometallic crystals. *Science* 168:568–70

54. Lawrence WE, Doniach S. 1970. In *Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto, 1970*, ed. E. Kandap. p. 361. Tokyo: Academic

55. Harper JME, Geballe TH, Di Salvo FJ. 1975. Heat capacity of 2H-NbSe2 at the charge density wave transition. *Phys. Lett. A* 54:27–28; Schwall RE, Stewart GR, Geballe TH. 1976. Low temperature specific heat of layered compounds. *J. Low. Temp. Phys.* 22:557–67

56. Wilson JA, Di Salvo FJ, Mahajan S. 1974. Charge density waves in metallic, layered, transition-metal dichalcogenides. *Phys. Rev. Lett.* 32:882–85

57. Beasley M, Geballe TH, King C, Hammond R, Norton R, et al. 1977. Electrical properties of multi-layered Nb$_3$Sn superconducting power line conductors. *IEEE Trans. Mag.* 13:138–143

58. Dayem AH, Geballe TH, Zubeck RB, Hallak AB, Hull GW Jr. 1978. Epitaxial growth of Nb3Ge on Nb3Ir and Nb3Rh. *J. Phys. Chem. Solids* 39:529–38

59. Feldman R, Hammond RH, Geballe TH. 1986. Epitaxial growth of A$_{15}$ Nb$_3$Si. *IEEE Trans. Mag.* 17:545–48; Feldman RD, Opila RL, Geballe TH, Celaschi S. 1986. Unusual variability of the lattice constant in polycrystalline epitaxial growth of superconducting A$_{15}$ Nb-Si. *Thin Solid Films* 137:315–24

60. Kimhi DB, Geballe TH. 1980. Superconducting tunneling in the amorphous transition metals Mo and Nb. *Phys. Rev. Lett.* 45:1039–42

61. Bradley RM, Harper JME, Smith DA. 1986. Theory of thin-film orientation by ion bombardment during deposition. *J. Appl. Phys.* 60:4160–64

62. Wang CP, Do KB, Beasley MR, Geballe TH, Hammond RH. 1997. Deposition of in-plane textured MgO on amorphous Si3N4 substrates by ion-beam-assisted deposition and comparisons with ion-beam-assisted deposited yttria-stabilized-zirconia. *Appl. Phys. Lett.* 71:2955–57

63. Hammond RH, Peng LSJ, Wang W, Jo W, Ohnishi T, Beasley MR. 2006. Film growth at low pressure mediated by liquid flux and induced by activated oxygen. *US Patent Appl. 20070042127*

64. Yoshizumi S, Geballe TH, Kunchur M, McLean WL. 1988. Magnetoresistance of amorphous Mo$_x$Ge$_{1-x}$ near the metal-insulator transition. *Phys. Rev. B* 37:7094–97

65. Yoshizumi S, Carter W, Geballe TH. 1984. Flux-pinning and inhomogeneities or defects in amorphous superconducting Mo5Ge3 films. *J. Non-Cryst.Solids* 61-62:589–94
66. Carter WL, Poon SJ, Hull GW Jr, Geballe TH. 1981. Enhanced critical field curves of metastable superconductors. *Solid State Commun.* 39:41–45
67. Lowe WP, Geballe TH. 1984. NbZr multilayers. I: structure and superconductivity. *Phys. Rev. B* 29:4961–68
68. Broussard PR, Geballe TH. 1988. Superconductivity and structure in sputtered Nb-Ta multilayers. *Phys. Rev. B* 37:60–67
69. Eom CB, Marshall AF, Suzuki Y, Boyer B, Pease RFW, Geballe TH. 1991. Absence of weak-link-behaviour in $YBa_2Cu_3O_7$ grains connected by 90° (010) twist boundaries. *Nature* 353:544–47
70. Venkatesan T, Wu XD, Inam A, Jeon Y, Croft M, et al. 1988. Nature of the pulsed laser process for the deposition of high Tc superconducting thin films. *Appl. Phys. Lett.* 53:1431–33
71. Koster G, Kropman BL, Rijnders GJHM, Blank DHA, Rogalla H. 1998. Influence of the surface treatment on the homoepitaxial growth of SrTiO3. *Mater. Sci. Eng. B* 56:209–12
72. Ohtomo A, Hwang H. 2004. A high-mobility electron gas at the LaAlO3/SrTiO3 heterointerface. *Nature* 427:423–26
73. Fork DK, Fenner DB, Barrera A, Phillips JM, Geballe TH, et al. 1991. Buffer Layers for high-quality epitaxial YBCO films on Si. *IEEE Trans. Appl. Supercond.* 1:67–73; Fork DK, Char K, Bridges F, Tahara S, Lairson B, et al. 1989. YBCO films on YSZ and Al_2O_3 by pulsed laser deposition. *Phys. C* 162-164:121–22
74. Hellman ES, Schlom DG, Missert N, Char K, Harris JS, et al. 1988. Molecular-beam epitaxy and deposition of high-Tc superconductors. *J. Vac. Sci. Technol. B* 6:799–803
75. Eckstein JN, Bozovic I, von Dessonneck KE, Schlom DG, Harris JS, Baumann SM. 1990. *Appl. Phys. Lett.* 57:931–33
76. Bozovic I, Logvenov G, Verhoeven MAJ, Caputo P, Goldobin E, Geballe TH. 2003. No mixing of superconductivity and antiferromagnetism in a high-temperature superconductor. *Nature* 422: 873–75
77. Bozovic I, Eckstein JN, Klausmeier-Brown ME, Virshup G. 1992. Superconductivity in epitaxial Bi2Sr2CuO6/Bi2Sr2CaCu2O8 superlattices: The superconducting behavior of ultrathin cuprate slabs. *J. Supercond.* 5:19–23
78. Kihlstrom KE, Hammond RH, Talvacchio J, Geballe TH, Green AK, Rehn V. 1982. Preparation, tunneling, resistivity, and critical current measurements on homogeneous high-Tc A15 Nb_3Ge thin films. *J. Appl. Phys.* 53:8907–14
79. Kwo J, Geballe TH. 1981. Superconducting tunneling into the A15 Nb_3Al thin films. *Phys. Rev. B* 23:3230–39
80. Kihlstrom KE, Mael D, Geballe TH. 1984. Tunneling $\alpha 2F(\omega)$ and heat capacity measurements in high-Tc Nb_3Ge. *Phys. Rev. B* 29:150–58
81. Early SR, Hellman F, Marshall J, Geballe TH. 1981. A silicon on sapphire thermometer for small sample low temperature calorimetry. *Physica B&C* 107:327–28
82. Hellman F, Geballe TH. 1987. Specific heat of thin-film A15 superconductors: an anomalous in-homogeneity discovered. *Phys. Rev. B* 36:107–20
83. Rudman DA, Beasley MR. 1984. Microscopic superconducting parameters from tunneling in A15 Nb-Sn. *Phys. Rev. B* 30:2590–94
84. Labbe J, Friedel J. 1966. Stabilité des modes de distorsion périodiques d'une chaine linéaire d'atomes de transition dans une structure cristalline du type V 3Si. *J. Phys. France* 27:708–16
85. Weger M, Goldberg JB. 1973. Some lattice and electronic properties of the β-tungstens. *Solid State Phys.* 28:1–177
86. Chu CW, Rusakov AP, Huang S, Early S, Geballe TH, Huang CY.1978. Anomalies in cuprous chloride. *Phys. Rev. B* 18:2116–23
87. Chu CW, Early S, Geballe TH, Huang CY. 1978. Study of cuprous chloride under pressure. *J. Less Common Met.* 62:463–67
88. Geballe TH, Chu CW. 1979. Interface superconductivity in CuCl? *Comments Solid State Phys.* 9:115–26

89. Osipov VV, Kochev IV, Naumov SV. 2001. Giant electric conductivity at the CuO-Cu interface: HTSC-like temperature variations. *JETP* 93:1082–90

90. Siemons W, Koster G, Blank DHA, Hammond RH, Geballe TH, Beasley MR. 2009. Tetragonal CuO: end member of the 3d transition metal monoxides. *Phys. Rev. B* 79:195122

91. Munakata K, Geballe TH, Beasley MR. 2011. Quenching of impurity spins at Cu/CuO interfaces: an antiferromagnetic proximity effect. *Phys. Rev. B* 84:161405R

92. Kapitulnik A, Kent AD, Geballe TH, Kaufman JH. 1987. In *Novel Superconductivity*, pp. 61–71, ed. S Wolf, VZ Kresin. New York: Plenum Publ. Corp.

93. Bednorz JG, Müller KA. 1986. Possible high T_c superconductivity in the Ba-La-Cu-O system. *Z. Physik B* 64:189–93

94. Uchida S, Takagi H, Kitazawa K, Tanaka S. 1987. High Tc superconductivity of La-Ba-Co oxides. *Jpn. J. Appl. Phys.* 26:L1–2

95. Wu MK, Ashburn JR, Torng CJ, Hor PH, Meng RL, et al. 1987. Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure. *Phys. Rev. Lett.* 58:908–10

96. Lew D, Suzuki Y, Eom CB, Lee M, Triscone J-M, et al. 1991. Vertical transport properties of A-axis oriented YBa2Cu3O7/PrBa2Cu3O7/YBa2Cu3O7 sandwich junctions. *Physica C* 185-189: 2553–54

97. Kwo J, Hammond RH, Geballe TH. 1980. Nb3Al thin-film synthesis by electron-beam coevaporation. *J. Appl. Phys.* 51:1726–32

98. Sasaki S, Watanabe S, Yamada Y. 2007. Superconductivity driven by zigzag chain in Pr-based copper oxide evidenced by Cu-nuclear resonance. *J. Magn. Magn. Mater.* 310:696–97

99. Berg E, Geballe TH, Kivelson SA. 2007. Superconductivity in zigzag CuO chains. *Phys. Rev. B* 76:214505

100. Geballe TH, Moyzhes BY. 2004. Why the cuprate superconductors are unusual: an ionic approach. *Ann. Phys.* 13:20–26

101. Jin S, Tiefel TH, McCormack M, Fastnacht RA, Ramesh R, Chen LH. 1994. Thousandfold change in resistivity in magnetoresistive La-Ca-Mn-O films. *Science* 264:413–15

102. Snyder GJ, Hiskes R, DiCarolis S, Beasley MR, Geballe TH. 1996. Intrinsic electrical transport and magnetic properties of $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ MOCVD thin films and bulk material. *Phys. Rev. B* 53:14434–44

103. Worledge DC, Geballe TH. 2000. Spin-polarized tunneling in La0.67Sr0.33MnO3. *Appl. Phys. Lett.* 76:900–2

104. Meservey R, Tedrow PM. 1994. Spin-polarized electron tunneling. *Phys. Rep.* 238:173–243

105. Worledge DC, Geballe TH. 2000. Magnetoresistive double spin filter tunnel junction. *J. Appl. Phys.* 88:5277–79

106. Miao G-X, Müller M, Moodera JS. 2009. Magnetoresistance in double spin filter tunnel junctions with nonmagnetic electrodes and its unconventional bias dependence. *Phys. Rev. Lett.* 102:076601

107. Nemov SA, Ravich YI. 1998. Thallium dopant in lead chalcogenides: investigation methods and peculiarities. *Physics-Uspekhi* 41:735–59

108. Anderson PW. 1975. Model for the electronic structure of amorphous semiconductors. *Phys. Rev. Lett.* 34:953–55

109. Matsushita Y, Bluhm H, Geballe TH, Fisher I. 2005. Evidence for charge Kondo effect in superconducting Tl-doped PbTe. *Phys. Rev. Lett.* 94:157002

110. Erickson AS, Breznay NP, Nowadnick EA, Geballe TH, Fisher IR. 2010. Correlation of anomalous normal state properties with superconductivity in $Pb_{1-x-y}Tl_xIn_yTe$. *Phys. Rev. B* 81:134521-1–6

111. Dzero M, Schmalian J. 2005. Superconductivity in charge Kondo systems. *Phys. Rev. Lett.* 94:157003

112. Costi TA, Zlatić V. 2012. Charge Kondo anomalies in PbTe doped with Tl impurities. *Phys. Rev. Lett.* 108:036402

113. Terada N, Iyo A, Tanaka Y, Obara K, Ihara H. 2001. Photoemission Study of (Cu, Tl)-1223 and Tl-1223 with Tc above 130 K. *IEEE Trans. Appl. Supercond.* 11:3126–29

114. Iyo A, Tanaka Y, Kodama Y, Kito H, Tokiwa K, Watanabe T. 2006. Synthesis and physical properties of multilayered cuprates. *Physica C* 445-448:17–22

115. Raghu S, Thomale R, Geballe TH. 2012. Optimal Tc of cuprates: the role of screening and reservoir layers. *Phys. Rev. B* 86:094506

116. Hiroi Z, Takano M, Azuma M, Takeda Y. 1993. A new family of copper oxide superconductors $Sr_{n+1}Cu_nO_{2n+1+\delta}$ stabilized at high pressure. *Nature* 364:315–17

117. Han PD, Chang L, Payne DA. 1994. High-pressure synthesis of the Sr2CuO3+δ superconductor observation of an increase in Tc from 70 K to 94 K with heat treatment. *Physica C* 228:129–36

118. Zhang H, Wang YY, Marks LD, Dravid VP, Han PD, Payne DA. 1995. A TEM study of the incommensurate modulated structure in Sr2CuO3+x superconductors synthesized under high pressure. B. Structural model. *Physica C* 255:257–65

119. Wang YY, Zhang H, Dravid VP, Marks LD, Han PD, Payne DA. 1995. A TEM study of the incommensurate modulated structure in Sr2CuO3 + δ superconductor synthesized under high pressure. A. Evolution of the incommensurate modulated structure and the electronic structure with post-heat treatment. *Physica C* 255:247–56

120. Liu QQ, Yang H, Qin XM, Yu Y, Yang LX, et al. 2006. Enhancement of the superconducting critical temperature of $Sr_2CuO_{3+\delta}$ up to 95 K by ordering dopant atoms. *Phys. Rev. B* 74:100506R

121. Geballe TH, Marezio M. 2009. Enhanced superconductivity in Sr_2CuO_{4-v}. *Physica C* 469:680–84

122. Chmaissem O, Grigoraviciute I, Yamauchi H, Karppinen M, Marezio M. 2010. Superconductivity and oxygen ordering correlations in the homologous series of $(Cu, Mo)Sr_2(Ce, Y)_sCu_2O_{5+2s+\delta}$. *Phys. Rev. B* 82:104507

123. Hwang HY, Iwasa Y, Kawasaki M, Keimer B, Nagaosa N, Tokura Y. 2012. Emergent phenomena at oxide interfaces. *Nat. Mat.* 11:103–13

124. Berg E, Orgad D, Kivelson S. 2008. Route to high-temperature superconductivity in composite systems. *Phys. Rev. B* 78:094509-1–7

125. Taraphder A, Krishnamurthy HR, Pandit R, Ramakrishnan TV. 1995. Negative-U extended Hubbard model for doped barium bismuthates. *Phys. Rev. B* 52:1368–88

126. Geballe TH. 2006. The never-ending search for high-temperature superconductivity. *J. Supercond. Novel. Magn.* 19:261–76

127. Gamble FR, Osiecki JH, Cais M, Pisharody R, Di Salvo FJ, Geballe TH. 1971. Intercalation complexes of Lewis bases and layered sulfides: a large class of new superconductors. *Science* 174:493–97