



Theodore H. Geballe

# Why I Haven't Retired

Theodore H. Geballe

Departments of Applied Physics and Materials Science, Stanford University, Stanford, California 94305; email: geballe@stanford.edu

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## 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  $\text{H}_2\text{O}$ , was  $\text{H}_2\text{SO}_4$ .” 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 Mozyhes 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 Giaque’s lab during my senior year. Giaque’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. Giaque 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 Giaque’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. Giaque'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 Giaque'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 Giaque'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 Giaque 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  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , partly because  $\text{Cu}^{++}$ , 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. Giaque 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).

Giaque, as a young faculty member in 1924, had calculated from susceptibility data of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , 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  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  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  $R \ln 2$  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 Giaque 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.<sup>1</sup> 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.

<sup>1</sup>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.<sup>2</sup>

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  $\sim kT$ ,

<sup>2</sup>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%  $\text{Ge}^{74}$ -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  $\sim 2 \times 10^{18} \text{ cc}^{-1}$ ) 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  $\sim 10^{16} \text{ cc}^{-1}$ ), 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 ( $\sim 10^{14} \text{ cc}^{-1}$ ) 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 ( $\sim 100,000,000$ -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  $\text{LaRh}_5$  were found to precipitate from a  $\text{La}_{0.01}\text{Rh}_{99}$  melt and to form a scaffold with connected  $\text{LaRh}_5$  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 ( $\text{La}_{0.001}\text{Rh}_{999}$ ) gave broad zero-field cooled signals. Transition electron microscopic images showed that in this latter case, the superconducting filaments of  $\text{LaRh}_5$  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  $\text{LaRh}_5$  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  $\mu^*$  that is of the opposite sign and of sufficient magnitude to roughly cancel the pre-exponential energy factor  $\omega_0$  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  $\sim 1$  K. The Fe is a pair breaker that reduces  $T_c$  at a record rate of  $\sim 100$  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  $\text{LaMnO}_3$  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  $\text{SrTiO}_3$  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  $\text{K}_x\text{WO}_3$  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  $\sim 90$  K later reported in  $\text{Na}_x\text{WO}_3$  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  $T_{\text{cmax}}$  of  $\sim 13$  K) in  $\text{BaBiO}_3$ , 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  $\sim 30$  K when  $\text{BaBiO}_3$  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  $\text{WO}_3$  bronzes discussed above, the pairing in  $\text{BaBiO}_3$  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.

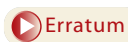
I have often been asked what the difference is between the Applied Physics and the Physics departments. The two departments have many common intellectual interests including superconductivity. The distinction is that Applied Physics is also engaged in possible technological applications,<sup>3</sup> 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.<sup>4</sup>

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**).

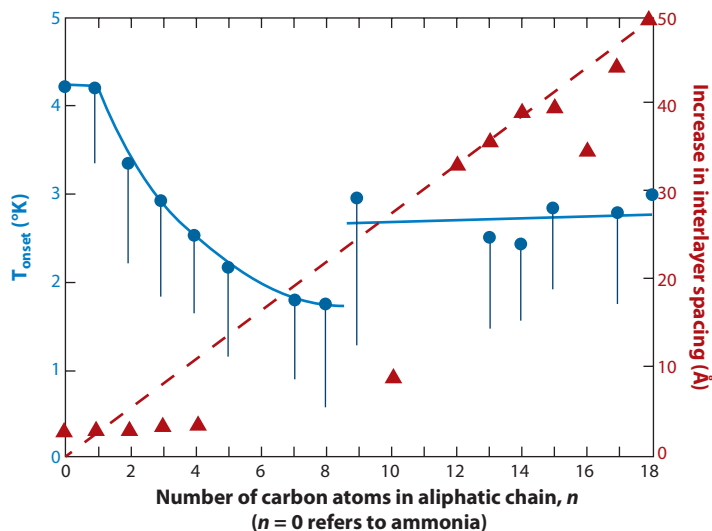
The Lawrence-Doniach model of 2D Josephson tunneling (54) shows why  $T_c$  could be independent of the spacing. A nice experimental demonstration is shown in **Figure 1**. The intriguing increase in  $T_c$  upon the intercalating TaS<sub>2</sub> with ammonia that I had hoped might be the signal of an 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



<sup>3</sup>The formation of Conductus, a start-up company, is an example discussed below.

<sup>4</sup>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  $\text{CH}_3\text{-(CH}_2\text{)}_{(n-1)\text{-NH}_2}$ . 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  $\text{Nb}_3\text{Sn}$  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

$\text{Mo}_x\text{Ge}_{1-x}$  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  $90^\circ$  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  $\text{TiO}_2$ -terminated surfaces on  $\text{SrTiO}_3$  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,  $\text{SrTiO}_3$  and  $\text{LaAlO}_3$ , 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,  $\text{CuO}_2$  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  $\text{Nb}_3\text{Sn}$  (83),  $\text{Nb}_3\text{Al}$  (79), and  $\text{Nb}_3\text{Ge}$  (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  $\text{CuCl}$ . 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  $\text{Cu}^{+1} = \text{Cu} + \text{Cu}^{+2}$ . 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  $\text{La}_2\text{S}_3$  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  $\sim 30$  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  $\text{Hi}T_c$  research that followed.<sup>5</sup> We were soon able to capitalize on our experience with epitaxial growth and used  $\text{SrTiO}_3$  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  $\text{CuO}_2$  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  $\text{CuO}_2$  layers. Moreover, it has

<sup>5</sup>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 ( $\text{HgO}_x$ ,  $\text{TlO}_x$ , or  $\text{BiO}$ ) were inserted between the  $\text{SrO}$  layers in optimally doped 214  $(\text{LaSr})_2\text{CuO}_4$ , 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  $\text{CuO}_2$  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  $\text{CuO}$  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  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (102).  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3/\text{SrTiO}_3/\text{Al}$  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<sup>6</sup> when substituted for divalent Pb in semiconducting  $\text{PbTe}$  (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:  $2\text{Tl}^{+2} \Rightarrow \text{Tl}^{+1} + \text{Tl}^{+3}$ . At the lowest concentration of Tl that induces superconductivity in  $\text{PbTe}$ ,  $\sim 0.3\%$ , 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  $\text{CuO}_2$  layers of Hg and Tl cuprates. It would be an unlikely

<sup>6</sup>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  $\text{Sr}_2\text{CuO}_{(4-v)}$  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  $(\text{Cu}_{.75}\text{Mo}_{.25})-12\text{s}2$ . For  $s = 1$ ,  $T_c = 87$  K, and the Cu valence in the  $\text{CuO}_2$  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  $\text{CuO}_2$  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  $(\text{CeY}-\text{O}_2-\text{CeY})_{s-1}$  fluorite layers between the two  $\text{CuO}_2$  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  $\text{SrTiO}_3$  and insulating  $\text{LaAlO}_3$  (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,  $\Delta$ , 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  $\text{BaBiO}_3$  (125), the physics could be related to that described above for  $(\text{PbTi})\text{Te}$ .

A few intriguing USOs, such as metastable  $\text{CuCl}$  and  $\text{CuO}$ , 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.

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I am not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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