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WALTER DAVID KNIGHT
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A Biographical Memoir by

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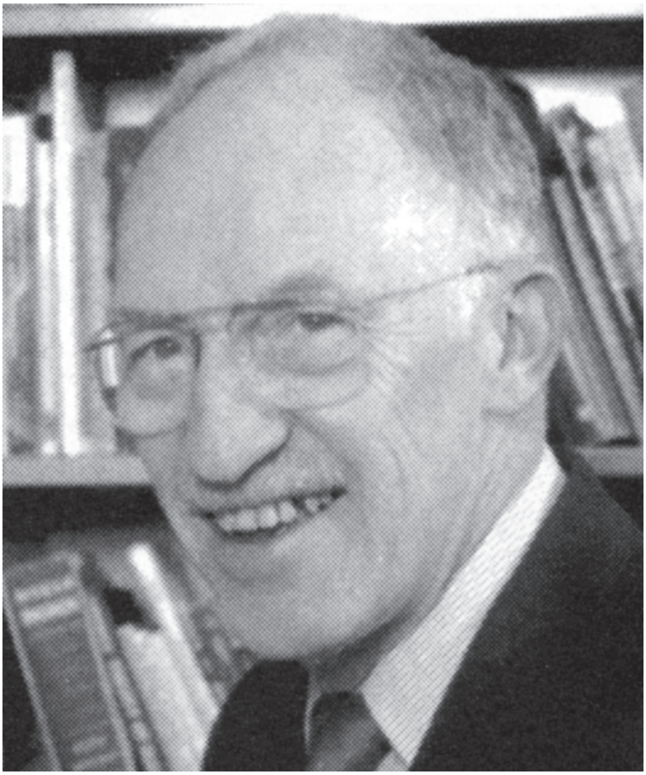

WALTER DAVID KNIGHT

October 14, 1919–June 28, 2000

BY ERWIN L. HAHN, VITALY V. KRESIN, AND
JOHN H. REYNOLDS

WALTER DAVID KNIGHT was a consummate experimental physicist. His 50 years of research spanned widely different techniques, albeit with a central focus on the physics of metals. His first experiments were with test tube-like samples at room temperature and atmospheric pressure. The electronics and magnets were homemade; the data emerged as red ink tracings of galvanometer deflections on long strips of paper. Unafraid of a whole new world of techniques, he much later carried out experiments on samples of clustered metallic atoms, produced in vacuum by supersonic jets of argon and analyzed in molecular beams. There his complex apparatuses were computer controlled, and the data emerged into digital files.

Walter's name has been immortalized in condensed-matter physics as the discoverer of a nuclear magnetic resonance phenomenon known as the "Knight shift." It was a major development in the understanding of the electronic properties of metals, and to this day remains a mainstay tool in research on metals, alloys, and superconductors. He pio-

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neered the use of electric quadrupole resonance as well as magnetic resonance as probes of structural and electronic effects, phase transitions, liquid metals, etc.

Later in his career he initiated groundbreaking work on the physics of small metal clusters, now referred to as nanoclusters. His group discovered their electronic shell structure and traced the evolution of their metallic properties with increasing size. The field of nanoparticle science has blossomed in the past 20 years, and Walter Knight is acknowledged as one of its pioneers.

His 40-year career at the University of California, Berkeley, also involved a continuing full load of teaching and for a time extraordinary service as an academic dean.

FROM BOYHOOD TO THE DOCTORATE

Walter was born October 14, 1919, and was raised mostly in New York City. His father was a leading Presbyterian minister, who was able to maintain a comfortable home in the city and to send Walter and his sister, Paula, to excellent schools. The Knight family, however, hailed from a farming background in Marlborough, New Hampshire, and Walter spent his summers there as a country boy, "Ginger" Knight to his numerous cousins. New Hampshire had a deeper stamp on Walter than the big city, and his practicality with tools and his earthy sense of humor attested to that fact.

His college years were at Middlebury College in Vermont. His graduate work was at Duke University, where before his World War II military service as a radar officer in the U.S. Navy, he received an M.A. degree in physics and completed all the requirements for a Ph.D. except for the required research. He recalled that he had "plenty of training in electronics in the Navy" that stood him in good stead in his subsequent research. He wrote an interesting account of his immediate postwar research in a paper entitled "The Knight Shift," which appears in volume I of the *Encyclopedia of Nuclear Magnetic Resonance*, cited at the end of this memoir. There one reads about the events that led to his important discovery of the shift in nuclear magnetic resonance frequencies that occurs in metals and provides a probe of the local internal fields in materials without disturbing the basic structure of the system under study. The research for his Ph.D. thesis at Duke was carried out while Walter was an assistant professor of physics at Trinity College, Hartford, and while he was commuting to or "summering" at the Nuclear Moments Laboratory at Brookhaven National Laboratory, where his apparatus was put together. In practical matters of experimental technique he interacted closely at Brookhaven with Bill Cohen and Bob Pound. In the theoretical interpretation of his results he interacted closely with Norman Ramsey, Samuel Goudsmit, Conyers Herring, and perhaps most importantly, with Charles Townes, whom Walter sometimes described as his informal thesis supervisor.

EARLY RESEARCH AT BERKELEY

His successes in research brought him to the attention of Berkeley physics professor Francis Jenkins, who had been dispatched by other senior professors there to travel eastward and recruit new talent for the Physics Department, where a new addition to LeConte Hall was nearing completion and where expansion of the department had been authorized. One of Jenkins's assignments had been to recruit people who could establish a group in solid-state physics, hitherto unrepresented as a field at Berkeley. His success in this assignment can be gauged by the fact that he recruited Erwin Hahn, Carson Jeffries, Arthur Kip, Charles Kittel, and Walter Knight who eventually came to form the nucleus of this group.

Walter moved to Berkeley and began experimental work there in the summer of 1950. Walter's important discovery in Brookhaven of the effect of the magnetism of conduction electrons in metals on the nucleus had opened up an important subfield of research on nuclear magnetic resonance. With this new way available to study properties of electrons in conducting materials, Walter and his students at Berkeley contributed a series of pioneering investigations of many different types of conducting solids, including alloys, semiconductors, and superconductors. As these experiments evolved it was learned in more detail that the Knight shift had to be distinguished more carefully from other competing shifts. These were the chemical frequency shifts due to the action of chemical bonds, and nuclear electric quadrupole shifts occurring in non-cubic metals. Not only was the Knight shift an important parameter but also the theory behind it was closely connected with the parameter of nuclear spin-lattice relaxation times measured in metals. Because of the skin depth penetration limit of radio-frequency fields into the interior of metals, Walter and his students were often preoccupied in developing techniques to prepare metals in the form of very small spheres, with as much uniformity in diameter as possible.

Two very important research results came about. First, in the course of looking for the shift properties in non-cubic metals Walter and his students discovered the first nuclear quadrupole resonance in a metal, namely, gallium. They followed this discovery by seeing zero field quadrupole resonances in several other metals. Second, after the BCS theory of superconductivity in metals was introduced Walter exploited the Knight shift in such a way as to have it play an important experimental role in probing the BCS theory. The theory predicted that the Knight shift of the superconducting electrons should be reduced (that is, the spins should pair off more and more) as the temperature approached absolute zero. After overcoming a number of experimental artifacts, Walter confirmed that this reduction of the shift with temperature indeed did occur. (See also his narrative in the article from the *Encyclopedia of Nuclear Magnetic Resonance.*)

In addition to research papers Walter over the years wrote influential reviews. His 1956 review "Electron Paramagnetism and Nuclear Magnetic Resonance in Metals," published in *Solid State Physics*, vol. 2, p. 93, was designated a "citation classic" by Current Contents in 1985.

UNIVERSITY SERVICE AT BERKELEY

Walter, like most of his Berkeley colleagues, taught a full load of physics classes as a matter of course. In addition he consented to make one of his first contributions to university service as a so-called "baby dean" in the College of Letters and Science. There were several such deans assisting the principal dean of Letters and Science and their duties were mainly in interacting with students in the college and helping to solve the difficulties that students encounter in navigating their ways through the degree requirements and minimum scholastic achievements expected in the college. In 1963-64 an active issue arose at Berkeley as to how to decide which applicants to undergraduate status at Berkeley should be chosen among a large excess over the number of places available. The mechanism that seemed to be in ascendancy among the various proposals was the so-called "random selection," whereby places would be awarded in some sort of lottery. To Walter this device seemed so idiotic that he uncharacteristically became a campus activist against random selection and soon emerged as the leader of a successful faculty protest. His having served from 1961 to 1963 as an associate dean in the college, a step up from "baby dean," together with his newly recognized prominence as a faculty leader, led to his being named in 1967 as the principal dean of the College of Letters and Science. Suddenly Walter was serving in a job where all academic appointments at Berkeley, other than in the professional schools, were his to allocate (and help evaluate) among the many departments he oversaw. As well, he had to deal with the countless faculty dissatisfactions and frictions that arise so often in academia. For five full years Walter was in this administrative hot seat and pretty much on his own, because it was only upon his leaving that office that associate deans in the college, one to each of the four disciplinary branches, were assigned many of his responsibilities. One way of saying this is that when he retired as dean, the job was assumed not by one but five people. The years of his deanship, from 1967 to 1972, were beset with extra difficulties encompassing, as they did, strident times of student unrest at Berkeley and elsewhere in the United States.

RESEARCH AT BERKELEY AFTER HIS DEANSHIP

We believe it fair to say that seldom do academics who have to become so immersed in campus administration that their teaching and research is brought to a virtual standstill emerge from such service and return successfully to a combination of classroom teaching and significant research. So here begins a truly remarkable chapter in Walter's career, namely, two decades of groundbreaking work on the physics of small metal clusters.

Walter's first involvement with small metallic particles goes back to his work in the 1960s on the Knight shift in superconductors. Later in that decade he became very interested in the possibility of observing quantum size effects in small systems (or nanoclusters, as they are often referred to nowadays). The issue of energy level separation in small particles was first considered by Fröhlich in 1937 and was given great stimulation by a landmark paper of Kubo in 1962. It was predicted that for temperatures $k_B T < \delta$, where δ is the average electron level spacing, particle susceptibilities would be strongly altered and would display dramatic even-odd alternations. Walter's group began low-temperature nuclear magnetic resonance studies of 10- to 100-nm particles deposited on substrates and obtained results supporting the theoretical ideas.

They also came to realize that matrix interactions and associated problems prevented a clear view of quantum size effects. The path that Walter decided to follow to resolve this problem is nicely outlined on the last page of a 1975 paper by Yee and Knight.

> It therefore appears important to design complementary experiments which eliminate the problems of impurities and boundary interactions with the matrix at the surface of the particles under study. Such an experiment has been proposed and is being carried out in this laboratory . . . Beams of freshly condensed particles are formed by an oven and collimating slits and pass through an inhomogeneous magnetic field, as in the Stern-Gerlach experiment, to a detector. It appears to be quite feasible to employ particles in the range from 10 to 1000 atoms, thus making accessible a large range of measurements capable of elucidating the development of the electronic structure of the semi-infinite metallic lattice from the primordial metallic molecule . . . Ultimately, it should be possible to observe the effects of surface contamination and measure the heat capacity of the particles. The method is applicable to non-metallic particles . . . Electric deflections should be possible.

Today, 25 years after the appearance of this paper, it is remarkable that every single prospect outlined there has come to be realized and currently represents an active avenue of research.

Within the next several years the aforementioned cluster beam machine was indeed constructed (formed out of a big atomic beam apparatus donated by a department colleague), and beams of alkali-metal clusters were generated. This marked the transition of Walter's research from the world of solids and surfaces to that of beams, jets, and mass spectrometers. It also marked the first steps to a new discovery. Following initial experiments on Stern-Gerlach deflections of alkali trimers, the group proceeded to install a high-quality supersonic oven source and a high-range mass spectrometer in order to study larger clusters. A mass spectrum of sodium clusters spanning from 2 to 100 atoms was measured. A beautiful pattern appeared on the display: The cluster population did not form a simple featureless landscape, but instead resembled an impressive mountain range, with specific peaks (at 8-, 20-, 40-, 58-, and 92-atom sizes) especially prominent. It soon became apparent that these "magic numbers" were nothing less than a dramatic and long-sought manifestation of size quantization: shell ordering of the discrete states of delocalized electrons in small clusters. This observation is striking and beautiful, representing the third known appearance of shell structure in nature (after atoms and nuclei). Now it forms the basic framework for much of the work on understanding metal cluster evolution, a research enterprise that has grown from just a few groups in the late 1970s and early 1980s to many times that number today. Furthermore, it has established metal clusters as a fascinating laboratory for the accurate study of many-body physics. According to the Science Citation Index, by the end of 2002, the 1984 paper by Knight et al. on "Electronic Shell Structure and Abundances of Sodium Clusters" has been cited close to 900 times.

The discovery of shell structure was followed by a decade of further fundamental contributions by Walter, his students, and postdocs to the field of metal cluster physics. Space limitations prevent us from a detailed account of these results, so we shall only briefly mention benchmark measurements of cluster polarizabilities and ionization potentials, the landmark discovery of giant electronic resonances, or plasmons, in small clusters (the 1987-91 series of papers on this effect already share over 600 citations in the literature), and experiments on cluster scattering.

Walter enjoyed strong research ties with many colleagues around the world, including longstanding close contacts with cluster researchers at the Niels Bohr Institute in Copenhagen and at the École Polytechnique in Lausanne. He was undoubtedly pleased that his work on metal clusters has generated interest across so many research disciplines, attracting solid-state, atomic, chemical, and even nuclear physicists. (Shell effects analogous to those in metal clusters were recently discovered in the quantized conduction spectra of metal nanowires. This has potentially important practical consequences for nanoscale electronics and illustrates once more how beautiful results from basic research can lead in unpredictable ways to very useful applications.)

TEACHING AT BERKELEY

Walter reassumed his classroom teaching after serving as dean. Unlike many of his colleagues he *enjoyed* teaching the large lecture course in general physics designed for premedical students and the like. He taught it effectively for many years, bridging physics and liberal arts. With a friend in chemistry he also created an honors course in physical science that appealed to many of the brightest students in the arts. At a higher level of general physics Walter was a coauthor of the first volume of the Berkeley Physics Course, one of the U.S. curriculum-enrichment projects in the post-Sputnik era.

Between 1950 and 1991 Walter guided 29 graduate students to a doctorate in physics.

WALTER AND SARA

Walter was married in 1972 to Sara Pattershall Blanpied, a native of Maine. This union, a second marriage for both, was an exceptionally happy one. Between them Sara and Walter were parents to four children. Sara shared Walter's interests in the arts and became an active member of the campus and town community. Their home, high in the Berkeley Hills and commanding a breathtaking view of San Francisco Bay, was a gathering place for entertaining friends and colleagues, including visitors from the many places on the globe where researches and visits had taken the Knights. In this house one could always be assured of enjoying a superb glass of wine and truly wonderful conversation, friendly and erudite, full of love of art and history, nature and travel, music and science. Visiting this beautiful house and enjoying its genuinely warm hospitality was always a special experience.

We hope that this memoir will attest to the high regard that friends and colleagues had for Walter Knight, a son of New Hampshire whose work at Berkeley contributed so richly to science, to his university, and to his students.

WE WOULD LIKE to acknowledge the kind permission of Taylor & Francis, Ltd., to use the text of our biographical sketch published in a Festschrift for Walter Knight's eightieth birthday: *Philosophical Magazine B*, vol. 79, no. 9, 1999 (<http://www.tandf.co.uk>). We drew upon the recollections of Walter's friends, colleagues, and family, and upon his autobiographical article entitled "The Knight Shift" published in the *Encyclopedia of Nuclear Magnetic Resonance*, vol. 1, edited by D. M. Grant and R. K. Harris (Chichester: Wiley, 1995) and reprinted in the aforementioned Festschrift. We also made use of the UC Berkeley press release of June 30, 2000, by R. Sanders.

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