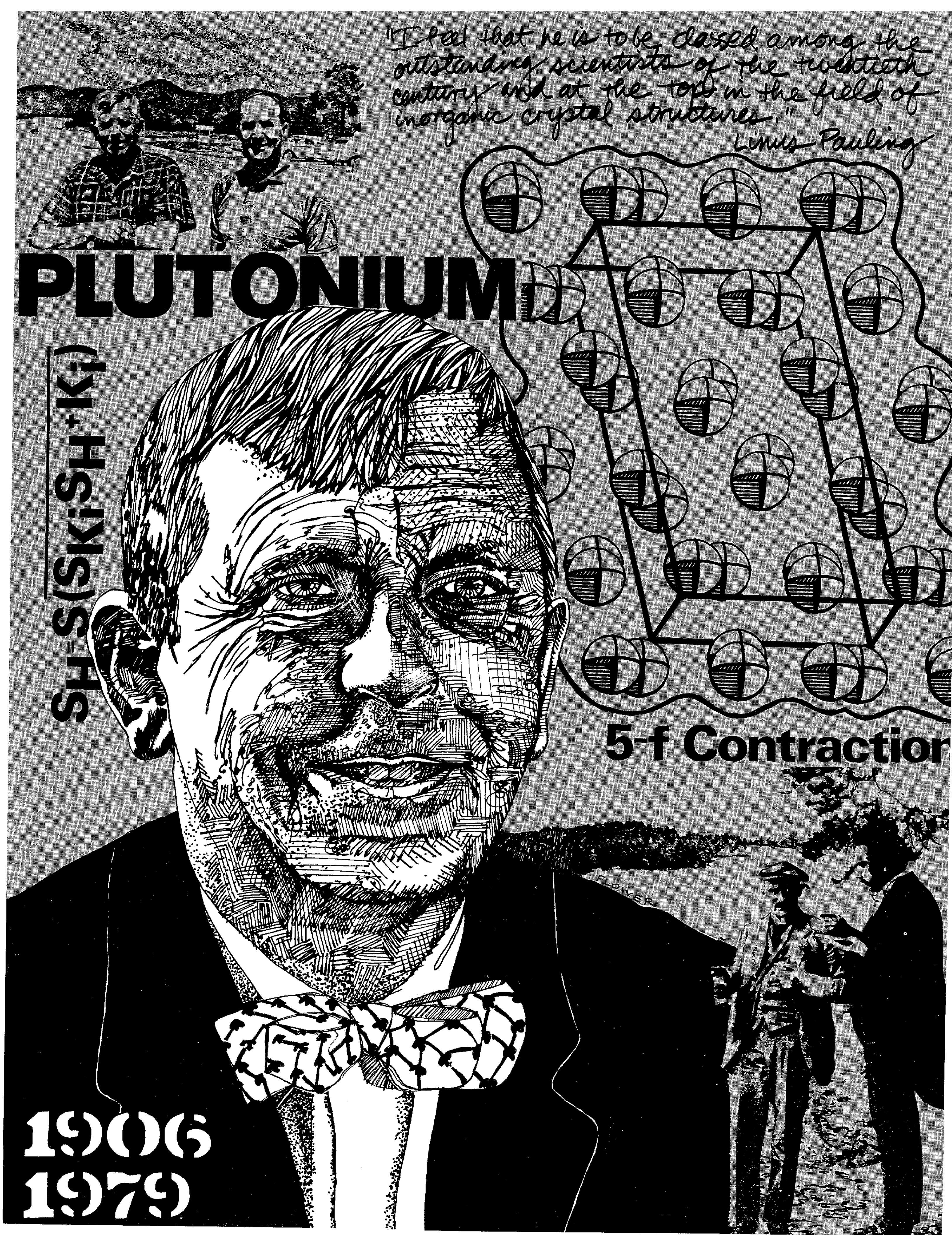


"I feel that he is to be classed among the outstanding scientists of the twentieth century and at the tops in the field of inorganic crystal structures."
Linus Pauling
PLUTONIUM
SH=S(SKiSH+Ki)
5-f Contraction
FLOWER
1906
1979

MEMORIAL TO

Professor (Fredrik) William H. Zachariasen

Born February 5, 1906, Langesund, Norway
Died December 24, 1979, Santa Fe, New Mexico

by Robert A. Penneman

Prof. Zachariasen, one of the outstanding scientists of the 20th Century, is gone. "Willie" leaves to his countless friends the warm remembrance of his gracious manner, his great good humor, and his generous friendship. His rich and varied scientific contributions engaged him to the last. He was one of the giants in x-ray crystallography and was involved in every major advance in that field. Linus Pauling wrote of him:

I have known Professor Zachariasen for nearly fifty years. His principal field of work has been the determination of the structure of crystals of inorganic substances by use of the x-ray diffraction technique. This is a field in which I also have done a large amount of work, and I believe that I am in a position to form a sound opinion about his ability and his contributions. It is my opinion that he has been and is the world leader in this field.

I feel that he is to be classed among the outstanding scientists of the twentieth century, and at the top in the field of inorganic crystal structures.

The Formative Years

Zachariasen began his career, unknowingly, with his youthful exploration of the islands in Langesundfjord near his home, islands rich in well-crystallized rare earth minerals. He was to return to those islands later as a student at the University of Oslo under the great geochemist Prof. Goldschmidt, who had purchased one of the islands for his studies. "Willie" rowed him out on occasion, a short journey for the son of a sea captain. The trips to the islands combined work with pleasure. Mrs. Zachariasen supplied a photograph of a picnic on one of the islands; in it Prof. Goldschmidt is seen talking to guest Albert Einstein. The vivid memory of those days never left Zachariasen; some dozens of years later he correctly identified (on sight) one of the crystal specimens from the Langesundfjord islands—a specimen that had been mislabeled by a commercial firm.

Zachariasen spent his student days (1923-1928) in the midst of that exciting period when Goldschmidt and his collaborators worked out general laws governing distribution of chemical elements in minerals; they were the first to apply x-ray diffraction to the study of geochemistry. During those years Zachariasen read hundreds of x-ray films, an activity that he continued throughout his life. Where the results were of particular significance, as in the recent controversy involving the α' and α'' phases of cerium, he would read each film several times.

Zachariasen published his first paper at age 19, after presenting it before the Norwegian Academy of Science the year before. It was on x-ray diffraction studies of oxides. With its publication in 1925 he began a period of contributions to the scientific literature, most of them singly authored, which would span 55 years. At age 22, he received his Ph.D., the youngest person ever to receive it in Norway. In 1928-29, he was a Postdoctoral Fellow at the laboratory of Sir Lawrence Bragg, where he began his study of silicate structures, a study that would later culminate in the first real understanding of the structure of glass. He returned to the University of Oslo, but within a year accepted a call from Nobel Laureate Arthur Compton to join the faculty of Physics at the University of Chicago. He was 24.

Before leaving Norway in 1930, he married Ragni Durban-Hansen, the striking granddaughter of the pioneer Norwegian geochemist, W. C. Brøgger, who discovered and first described the extensive mineral deposits of the Langesund area. Willie and his bride spent their honeymoon on the ship that brought them to the United States to fulfill his commitment to the University of Chicago. There he spent the next 44 years. The Zachariasens had two children, Fredrik Zachariasen (at the California Institute of Technology, Pasadena) and Ellen Z. Erickson of Santa Monica.

Zachariasen

Zachariasen (top). Prof. Goldschmidt and Albert Einstein at a picnic on the islands of Langesundfjord (bottom).

The University of Chicago

Many honors came to him during the 44 years at the University of Chicago, He advanced to full Professor, then to Department Head (during the critical post-war years when the department was rebuilt), and finally to Dean of the Physical Sciences. He was a kindly administrator and solicited advice, but always maintained a policy that one had to "select the few from the many." He was a member of the Norwegian Academy of Science, the U.S. National Academy of Science, the American Academy of Arts and Sciences, the American Physical Society, the American Crystallographic Association, and the Executive Committee of the International Union of Crystallography. He was presented with the honorary degree of Doctor of Science by the New York Polytechnic Institute.

The 1930s were years of financial hardship. Travel funds were nonexistent and Zach would sit up on a night train to New York, give his paper at a scientific meeting the next day, and return that night to save the cost of a hotel room. During that same period x-ray work was shut down for six months for lack of a $75 tube.

But those were also years of high scientific productivity. Following his work with silicates and other oxy-anions, Zachariasen began to think about how the glass structures were built. In 1932 he published his landmark paper on the structure of glass. Referring to this paper in 1961, Charles H. Green wrote: "The present day understanding of glass rests heavily on a singly lucid paper, only 12 pages long, written in 1932 by W. H. Zachariasen." Zachariasen continued through 1941 to study complex oxy-anions and to develop his work on the diffuse scattering of x rays caused by thermal motion.

In 1941 he became an American citizen. He was then in his mid-30s and already a world figure, having published 80 experimental and theoretical papers, including major papers on diffuse scattering, oxide structures, and the structure of glass. A significant change was soon to occur following the onset of World War II.

The War Years

In parallel with his academic career, Zachariasen began in 1943 to immerse himself in a then-secret activity, doing all the x-ray identification work for a new project on the Chicago campus. As part of a major wartime effort, scientists had gathered at the Metallurgical Laboratory to work with new elements that had not yet been seen, new elements whose chemistry was largely a mystery.

Recall the situation—Enrico Fermi had just demonstrated the existence of the chain reaction at Chicago in December 1942, using uranium.* Plans were being rushed for the pilot plant at Oak Ridge, Tennessee, and the production reactors at Hanford, Washington. This meant that the new element, plutonium, would be made in large quantity using neutrons from a nuclear reactor. Before this, plutonium could be made only in microgram quantities by tedious cyclotron irradiation.

*During the Fall of 1942 I was in Massachusetts as part of the Chicago team aiding in the production of sufficiently pure uranium metal.

There still remained the formidable chemical separations problem. How could pounds of plutonium be isolated from tons of uranium containing radioactive fission products? Chemical processes had to be devised that would work efficiently on a large scale and in high-radiation fields that required remote handling. Ultimately, plutonium metal had to be made. What would be its properties? Totally unexpected were the great complexities soon to be encountered with the plutonium metal phases, their unusual number (six), and the confusion caused by the ease of transfer among the four plutonium aqueous valence states.

Seaborg, the co-discoverer with Kennedy, Segrè, and Wahl of the fissionable isotope ^{239}Pu, was responsible for directing the efforts of some 60 chemists attempting to elucidate its chemical properties and to develop reliable plutonium separation processes. This was a heavy responsibility and work was conducted with great urgency (July 4th was just another work day). Zachariasen's x-ray analyses provided the information essential to the understanding of plutonium chemistry, deciphering single-handedly the composition of countless samples that were prepared by the chemists. His work was indispensable in replacing mystery with fact and guesses with quantitative structure identification.

Zachariasen was uniquely equipped for this challenge, given his prodigious skill in elucidating structures from powder diffraction data, plus his long familiarity with the rare earths and their 4f-contraction [the decrease in size with increasing atomic number at constant oxidation state (valence)]. Zachariasen's application of crystallography to the elucidation of the nature and chemistry of the transuranic elements, their compounds and metals, is probably his most celebrated work, covering 37 years and several dozen papers.

In the introduction to a book, which did not (and now cannot) get beyond that preliminary stage, Zachariasen wrote:

In 1943 Pu metal and some compounds were prepared in microgram amounts; but the ultra-microchemical studies of plutonium presented great difficulties of interpretation. Because of the small amounts of material, it was difficult to prepare single phase samples and to establish chemical identities.

In the autumn of 1943 I demonstrated that satisfactory x-ray diffraction patterns of Pu-preparations on the 10 microgram scale could be obtained and that the interpretation of the x-ray pattern often could provide positive identification of the phase or phases present in the preparation. Thus, in the period from November 1943 to June 1944 a number of plutonium compounds were identified and their crystal structures determined in full or in part.

A fledgling chemist who was impressed by Zachariasen, and who later became an important crystallographer in his own right and Dean of Chemistry at Berkeley, David Templeton wrote:

Of those early days, I know from personal observation that Zachariasen's work strongly influenced the development of the separation processes for the Hanford plant. As a young chemist, quite unblemished with any understanding of crystallography, I heard him report to the Seaborg team the identity of this or that new compound as they tried to identify oxidation states. Zachariasen's identifications were almost the only reliable analyses available. He solved the structures of hundreds of substances... .

The 5f Series: Thorides vs Actinides

In "History of the Met. Lab, Section C-1," Seaborg recounts that on June 21, 1944, a sample of what was thought to be NpO_2 was sent to Zachariasen. By 11:00 A.M. on June 22, 1944, his x-ray analysis had confirmed the existence of NpO_2, and Zachariasen had written his memo discussing the thoride series. It states in part:

The radius of Np^{+4} is thus 0.015Å larger than that of Pu^{+4}, 0.016Å smaller than that of U^{+4}, and nearly identical with that of Ce^{+4}.

I believe that a new set of "rare earth" elements has made its appearance. I believe that the persistent valence is four, so that thorium is to be regarded as the prototype just as lanthanum is the prototype of the regular rare earth elements.

W. H. Zachariasen

There had been earlier qualitative observations supporting formation of a new inner transition series of elements; in particular, the narrow absorption features in the plutonium spectra suggested it. However, Zachariasen's quantitative data showing the progressive 5f contraction provided the key confirmation.

On July 14, Seaborg dictated a memo containing the sentence:"...I suggest that the elements heavier than actinium be placed in the Periodic Table as an 'Actinide Series'." The actinide name prevailed for the 5f series, but Zachariasen wrote, "The name actinide is not acceptable because thorium is never actinium-like... ." He called them the 5f-series and would point out that not until the elements 95 and 96 were the metals rare-earth-like, and that the dioxide structure persisted from ThO_2 to CfO_2, elements 90 through 98.

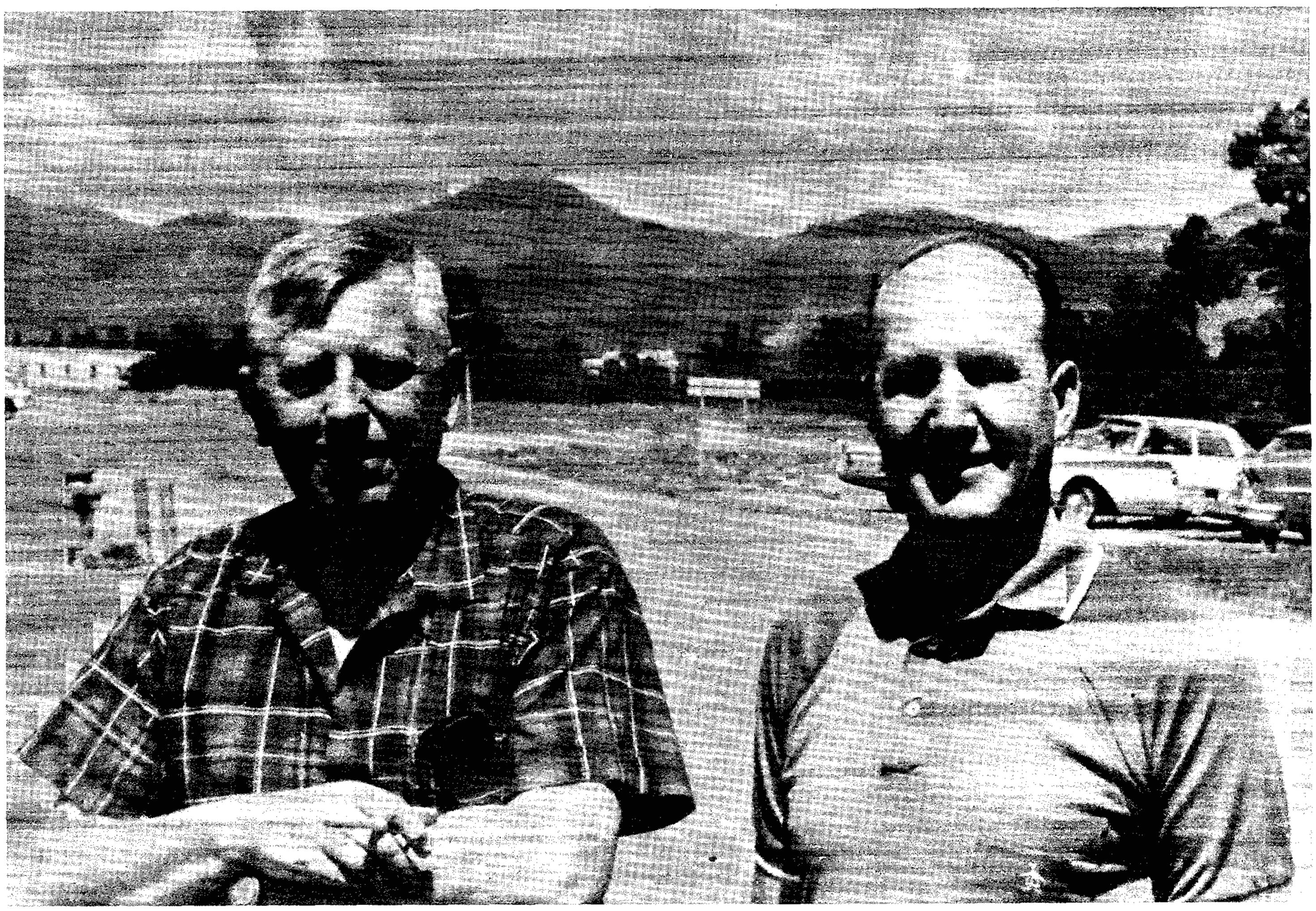
Twenty years earlier, Niels Bohr had predicted the occurrence of trans-uranium elements as a 5f series, with the series beginning at element 95. We now know conclusively that in the metals of this series, localized 5f electrons first appear with element 95 (americium) and in neighboring trivalent curium, element 96, the 5f shell is just half filled.

In an interview recounting those days and events pertaining to the history of Zachariasen's association with the University of Chicago, we find the following quotation with its significant ending:

... usually we found that the compounds which were present in the sample were not what they had intended to make. We had a very exciting time struggling with all these patterns over the various plutonium compounds, identifying what the chemists had made and, hence, getting information about the chemistry of plutonium that was essential... . I remember working like hell on New Year's Day and all holidays; often I worked late for many, many hours to get the work done. I had a wonderful time... .

Zachariasen

Willy Zachariasen and Bob Penneman in Los Alamos.



The Book

In 1945, Zachariasen published his classic and tightly written book, *The Theory of X-Ray Diffraction in Crystals.* Professor Pepinsky, himself a noted crystallographer, wrote of it: "The physical chapters serve as a basis for most of the developments in scattering theory since their publication; and many a contemporary paper is no more than a direct expansion of one or another paragraph." In 1948-49, Zachariasen published 26 papers, an heroic effort.

Direct Methods

In 1952, Prof. Zachariasen pioneered the use of "Direct Methods," for determining crystal structures. The extraction of detailed structural information from x-ray measurements requires the knowledge of two fundamental classes of information: the magnitudes and the phases of the structure factors. The values of the x-ray intensities are obtained directly, and are equal to the squared magnitude of the structure factors. For a complete solution of the structure, knowledge of the phases of the structure factors are necessary. Before 1952 the inability of the x-ray experiment to provide this latter information was referred to as the *phase problem.* This problem severely limited the application of the potentially powerful x-ray technique. The structure of solids containing small numbers of heavy atoms could be deduced more or less directly from the intensity pattern, but other substances were impossible to decipher except for the rare occasion when a model could be devised intuitively. The more powerful methods for deriving phase information depend on the statistical distribution of the intensities. This methodology is referred to as the *direct method* in crystallography.

In 1952 Zachariasen devised an algorithm for applications of this new method and successfully used it to determine the structure of boric acid. Although direct method techniques have been refined considerably in the ensuing years, Zachariasen's work remains the cornerstone of the modern methodology.

The Extinction Problem

In a series of brilliant papers published over the years 1963-1967, he described a practical solution to the problem of secondary extinction, one of the major unsolved problems in x-ray crystallography. Secondary extinction arises for reflections of such large intensity that an appreciable amount of the incident radiation is reflected by the first planes encountered by the beam. Since deeper planes are thus presented with less incident radiation, their reflections are reduced in intensity. This effect is strongly dependent on the types and degree of imperfections of the scattering crystal. The stronger the scattered intensity the more serious is the extinction. Scattered rays closest to the incident beam are generally most intense and it is specifically these low-angle reflections that are important in the accurate determination of valence electron distributions and the positions of light atoms such as hydrogen. In severe cases, secondary extinction problems can lead to erroneous results even in routine crystal structure determinations.

Some exceptionally accurate measurements on quartz caused Zachariasen to recognize a fundamental error made by diffractionist Darwin more than 50 years before in deriving the equations for the extinction effect. By the end of 1966, Zachariasen had circulated a preprint of a paper in which a practical solution to the extinction problem was described. It is a landmark of modern diffraction theory, ameliorating many of the problems that had held back precise structure determination.

Los Alamos Associations

In the early 1950s Zach began to consult at Los Alamos during the summers. During that period he accomplished a scientific *tour de force.* He succeeded in solving the complicated structures of plutonium metal, where others had labored fruitlessly even with computer assistance. In their book, *The Metal Plutonium*, Coffinberry and Miner state:

It is highly improbable that any scientist other than Zachariasen could have solved the three structures as complex as those of alpha, beta, and gamma plutonium from powder patterns alone.

He was simply unique in his ability to derive quantitative information from a powder diffraction pattern of a complex mixture. Often after what seemed like a glance, he would suggest cell size and composition. He had an uncanny knack for suggesting the correct atom positions. Only in recent years would he use a pocket calculator. He memorized trigonometric and log values to save time, and combined this with an incredible store of crystallographic information.

I was exposed to this ability and his extraordinary recall in 1953. We were then working with americium compounds. I showed him a film of one and he remarked, "Oh yes, I remember a similar pattern from an unknown plutonium compound, about six years ago." Our knowledge of the composition of the americium compound in combination with his x-ray data provided compositions and structures of both compounds. That was the beginning of a collaboration that continued, often including Larry Asprey, on the structures of the transplutonium metals. Zachariasen also continued his collaboration with Finley Ellinger and Fred Schonfeld. In such collaborations he never took offense in the rare instances when he was wrong and was able to offer guidance in such a tactful way that you were never offended.

With retirement from the University of Chicago and his move to Santa Fe in the 1970s, there were dinner parties given by Willie and Mossa (his pet name for her) in their Santa Fe home and gracious entertaining of friends from Santa Fe and Los Alamos. On the Hill there were parties involving the Agnews, Argos, Bradburys, Cowans, Evanses, Halls, Hoerlins, Hoyts, Kings, Marks, Matthiases, Metropolises, Richardsons, Rosens, Spences, Steins, Suydams, Tucks, Turkeviches, and Ulams. There were also poker sessions with a precise dichotomy: the *Chamber Music Society* allowed poker only in the purest form, while the *Symphony Society* permitted a wider variety of play.

For several years a Thursday ritual was established: Zach would come to Los Alamos to consult, first with Finley Ellinger and Fred Schonfeld in the morning; then after their lunch he would come to visit Larry Asprey, Bob Ryan, and me. In mid afternoon he would then go to the labs of Al Giorgi and Gene Szklarz, where he was invaluable in identifying the complicated mixtures involved in their superconductivity work. He went yearly to Bernd T. Matthias's lab in La Jolla for identification of minor but important components in the compounds that resulted from their search for high-temperature superconductors. That particular collaboration produced a series of important papers.

Recently he returned to the theme of 5f element bond lengths and bond strengths, providing the definitive tabulation of their values and simple equations to reproduce them.

A World Figure

On the world scene, in 1975 I had occasion to introduce Prof. Zachariasen at the Baden-Baden International Conference on Plutonium and The Other Actinides. I mentioned that he was then in his 50th year of publication, publishing his first paper before most in the audience were born. He received a standing ovation. In his self-effacing way he dismissed the tribute by saying, "I was born young." This year is his 55th year of contributing to the literature of science, and I shall always be proud of sharing in his final publication.

To an extent he was an anachronism, a scientific giant out of the times when science was funded from personal resources. For years, he paid his own way to meetings and was proud that he did not seek grants. Others took full advantage of the ready support for post-war science to build personal scientific empires. Zach did not; he felt it took the scientist-administrator too far from the science of the matter.

One measure of scientific impact is the extent that others make use of your work. It is scientific courtesy to acknowledge that debt by citing the former work. The system breaks down, because work of great importance often becomes just part of the lore and the more recent users are cited, not the original. This is true of Zach's work. Nonetheless, he was cited 3600 times in the period 1965-1975. This is an average of once for each day of that 10 years. It is clear that his name will remain bright in the literature of science.

To close, it is appropriate to repeat the quotation from Zachariasen's discussion of his arduous work during the war years, "I had a wonderful time."

Willie, so did those who know you!

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