Clarence M. Zener

1905–1993

BIOGRAPHICAL *Memoirs*

A Biographical Memoir by
John B. Goodenough

NATIONAL ACADEMY OF SCIENCES

CLARENCE MELVIN **ZENER**

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Solid-state physicist Clarence M. Zener, an influential pioneer in the field of materials engineering that blossomed after World War II, brought a deep curiosity and imaginative intuition to a wide range of fundamental scientific phenomena. The results brought not only transformative insights, but also produced innovations in numerous areas of practical application. His contributions included the Zener diode; magnetic oxides formed through Zener double exchange; calculation of diffusion in metals from internal-friction measurements; determination of the fracture strength of metals (as summarized in his seminal book *Elasticity and Anelasticity of Metals*); engineering optimization with geometric programming; and the identification of potential new technologies such as thermoelectric cooling and the green generation of electrical energy from the oceans. Further, Zener's insights tended to stimulate experimental inquiry and a new mode of thinking in virtually every field in which he worked.

By John B. Goodenough

Zener was born and raised in Indianapolis, Indiana. His early development was slowed by the death of his father near the time of his birth, an early stuttering problem, and difficulty learning to read before age 10, which kept him from being sent to a public primary school. But Zener's lack of early formal schooling shaped a confidence in self-learning and intellectual independence; it did not prevent him from developing the intellectual discipline that gave him entrance to Stanford University at age 16. Fascination with science from an early age, and his attraction more to mathematical concepts than to the exercise of calculation led Zener to major in mathematics at Stanford. After graduation in 1926, he went to Harvard University, earning his Ph.D. in physics under Edwin Kemble in 1929 with a thesis titled *Quantum Mechanics of the Formation of Certain Types of Diatomic Molecules*. Zener spent his postdoctoral years at Princeton University and the University of Bristol, England, exploring where his talents might be most effectively directed in the field of solid-state physics.

Before leaving Princeton to work with N. F. Mott and H. Jones at Bristol, Zener identified the possibility of a reverse-bias breakdown of a semiconductor diode. This could be accomplished by the tunneling of electrons across a heavily doped *p-n* junction from the n-doped to the *p*-doped side, where the reverse bias voltage is strong enough for the energy of the donor states of the *n*-doped side to cross the energy of the bottom of the *p*-doped conduction band. The voltage of this "Zener breakdown" can be varied from less than one volt to several hundred volts. The "breakdown diode" which is commonly called a Zener diode, is used as a voltage regulator.

In Bristol, Zener was engaged in the physics of metals, a field to which he would bring fundamental insights during his World War II years at the Watertown Arsenal in Massachusetts. While in England he also met and married Ruby Cross with whom he would have five children.

On his return from England, Zener taught physics at Washington University in St. Louis (1935–1937), the City College of New York (1937–1940), and Washington State University (1940–1942). He once remarked that he tended to flunk half of the undergraduate students he taught. When asked why, he would explain that a report from Reed College had pointed out that of those who majored in physics, the most successful later in life were the ones in the top 10 percent or the bottom 10 percent of the class. He felt that he was doing a favor to students who needed to be discouraged from pursuing a field in which they would end up as technicians at best.

During that period from the mid-1930s to the early '40s, Zener developed the field of internal friction with a series of papers on its theory and application. With simple oscillating strain measurements as a function of temperature, he obtained activation energies for the diffusion of solute atoms in metals, particularly carbon and nitrogen atoms in iron. This development and an associated paper, "A Method of Calculating Energy Losses During Impact" (Zener 1939), led to his call in 1942 to the Watertown Arsenal to develop stronger steel for the U.S. Army.

At the arsenal, Zener set himself to the problem of finding out why the existing steel fractured at low stress levels, in what ways the structure of steel had to be changed so as to raise the fracture stress, and how these changes could be brought about through improvements in the method of steel manufacture. With J. H. Hollomon, he first developed the concept of internal microcracks and how the reorientation of the microcracks by plastic deformation could explain curves of stress versus strain. In order to control the size of the microcracks in steel, Zener noted that iron undergoes a phase

transition from face-centered cubic to body-centered cubic on lowering the temperature from the melting point; and also that steel formation consists of two phases: (1) iron containing carbon and nitrogen; and (2) cementite, an iron carbide. A plate-like distribution of cementite precipitates increases the area of the microcracks, and constraining the cementite precipitates to spherical particles increases the stress at which steel fractures.

Control of the morphology and distribution of the cementite through carbon diffusion proved critical; Zener showed how this control through proper thermal processing could be achieved by satisfying two conditions: (1) the movement of the boundaries between the two iron phases is reversible; and (2) changes associated with the diffusion of carbon are irreversible. He also emphasized that the strain energy absorbed prior to fracture depends on the conditions of the strain-stress test (e.g., deformation by uniaxial tension versus torsion or deformation under tension versus hydrostatic pressure) while the thermodynamic variables controlling the fracture stress do not depend on these conditions. With Hollomon, he then went on to outline the research that would be needed to develop an understanding of anelastic deformation and fracture in metals—an agenda that has guided research to this day.

Carnegie Mellon University Archives.

At the war's end, Zener accepted a position as professor of solid-state physics at the University of Chicago (1945–1951). I arrived there in 1946 from service as a U.S. Air Force meteorologist. Four years later I managed to clear the hurdle of a 32-hour qualifying exam taken over four consecutive days, and I was interested in doing solid-state physics research under Zener. To my relief, he said, "I think you can be my student." Then he added, "Now you have two challenges; the first is to find a problem—a thesis topic— and the second is to solve it." In fact, Zener was helpful on both counts. Eventually, I found a problem, with his gentle guidance, that was not too trivial and not too hard for me to solve. But after several months working on my problem, I was stuck! Zener took it home to look at it over the weekend; he returned with a suggestion that helped me to move my problem forward.

At that time, Zener had finished his pioneering theoretical work on internal friction and was becoming intrigued by ferromagnetism, Néel ferrimagnetism, and a report of metallic conductivity in the oxoperovskites Na_xWO_3 and ferromagnetic $La_{1-x}Sr_xMnO_3$. Contemporary physicists assumed that the bonding in oxides was purely ionic, given that a point-charge model provided a nearly quantitative cohesive energy and that symmetry arguments provided interpretation of spectroscopic data with the crystal-field splittings as adjustable parameters. However, the transition-metal ions M in a perovskite are only coupled by M-O-M interactions that were thought to be 180° bonds; and interactions across an ionically bonded oxide ion presented a problem.

One morning Zener arrived excited with a new idea, which was typical for him. This time his idea was a "double-exchange" mechanism—to account for both the ferromagnetism and metallic conductivity of the perovskite $La_{1-x}Sr_xMnO_3$—that appeared to be consistent with purely ionic bonding with oxygen. Because $La_{1-x}Sr_xMnO_3$ contains, formally, mixed-valent Mn^{4+} and Mn^{3+} ions, he was proposing that the electron charge in the σ-bonding orbitals on high-spin Mn^{3+} ions is transferred to the empty σ-bonding orbitals on Mn^{4+} by displacing electrons from the intervening O^{2-} ions in a double-exchange process: Mn^{3+} to O^{2-} and O^{2-} to Mn^{4+}. Hund's intra-atomic exchange field would favor displacement of electrons with spins that were parallel to those on the acceptor Mn^{4+} ions. This electron transfer would be fast enough to eliminate the motional enthalpy for electron transfer. Although it is now known that real electron transfer across an oxide ion is the result of the covalent component of the M-O bond, it has been customary to refer to real electron transfer in a metallic oxide ferromagnet as Zener double exchange.

P. G. de Gennes would later carry the model one step further by introducing the angular dependence of the neighboring spin orientations, as first pointed out by P. W. Anderson. This model was generally accepted, without attention to the admonishment of Anderson that such a real charge transfer would not provide a ferromagnetic spin-spin interaction in the paramagnetic state and would not, therefore, give the ferromagnetic Weiss constant of the paramagnetic susceptibility that is observed experimentally. The real charge-transfer mechanism proposed by Zener, and as amended by de Gennes, was based on the assumption that the introduction of the covalent component of the M-O d-electron bonding accounts for the increased mobility of electrons in the ferromagnetically ordered phase and therefore also for magnetic polarons. But to account for a ferromagnetic Weiss constant in the paramagnetic susceptibility, the narrow band of σ-bonding itinerant electrons must be intrinsically ferromagnetic. Nevertheless, the

Zener proposal, typical of his insightful intuition, stimulated a great deal of experimental and theoretical work on ferromagnetic transition-metal oxides.

In 1951 Zener left the University of Chicago to accept the position of director of research at the Westinghouse Research Laboratory in East Pittsburgh. Consistent with his concern for and scientific generosity toward his students, Zener appointed as Westinghouse research engineer those of us in his group who had not yet completed their dissertation. When at Chicago, he and his wife Ruby had entertained us at their home on a Thanksgiving holiday, along with the family of a distinguished theoretical faculty member of the Physics Department, to expose us to an accomplished scientist in an informal setting. They continued this practice in East Pittsburgh by including us in an unforgettable evening at their home with E. J. W. Verwey, of the Philips Research Laboratory in Holland, who was visiting to talk with Zener about the Verwey transition in magnetite.

Carnegie Mellon University Archives.

In his new position, Zener felt compelled to create a materials research agenda with potential commercial payoff. On many weekends, he would come up with a new idea that he would peddle to a staff member in the hope that it would bear fruit. The problem was that another new idea would come before the young engine had figured out how to tackle the previous one. One visiting scientist from Germany figured out how to handle this problem. He would ignore the subsequent ideas until he could come up with an intelligent response to the first idea.

Toward the end of my year at Westinghouse, Zener came to me with the idea to use the thermoelectric power of doped NiO for airconditioning homes. This scheme, which would involve no moving parts, had a figure of merit given by $a^2\sigma/\kappa T$, where a is the thermoelectric power and σ/κ is the ratio of electronic to thermal conductivity.

I concluded that the Friedemann-Franz ratio σ/κ_e for electrons would defeat his scheme, but two other students, R. R. Heikes and R. W. Ure, Jr., argued that elimination of the lattice contribution to κ could save the day.

Zener then decided that the Westinghouse Research Laboratory was not the best environment for my talents, which gave me a month to submit my dissertation and find a new job. Nevertheless, Zener was generous with me at the last when Léon Brillouin, 10 days before my defense, challenged publicly the Brillouin zone that I had used in my dissertation. Devastated, I went to Zener, who encouraged me by saying he thought I had used the correct zone. With that support, I spent a weekend showing that Brillouin was mathematically correct and that the zone I had used was the appropriate one for my thesis, given that there in no energy discontinuity across the c-axis boundary of the first Brillouin zone.

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With regard to Zener's air-conditioning scheme, ultimately he was able to persuade the U.S. Navy to support it with 17 million dollars—a tidy sum in those days. At the end of this project, Zener's group had managed to come tantalizingly close to the practical figure of merit with bismuth telluride, and Heikes and Ure published a defining book on the work. This effort continues to stimulate ideas to develop material morphologies that may one day make Zener's idea commercially viable.

Another important Zener innovation at Westinghouse was his pioneering of geometric programming, an elegant optimization approach that remains an important tool in pure mathematics as well as in practical engineering and business-administration applications. Zener himself used geometric programming to model designs for heat exchangers, to perform ocean thermal energy conversion, and to discover the most suitable areas for its deployment.

Zener left Westinghouse to become dean of the College of Sciences at Texas A&M University, serving from 1965 to 1968. However, the university's administration did
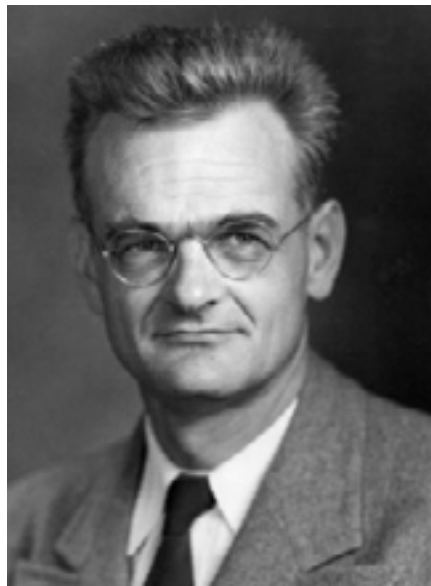
not give him time to employ his talent as an innovator of materials engineering. So he returned to teaching and research as University Professor of Physics at Carnegie Mellon University, where he remained until being taken by a heart attack in July 1993 at the age of 87.
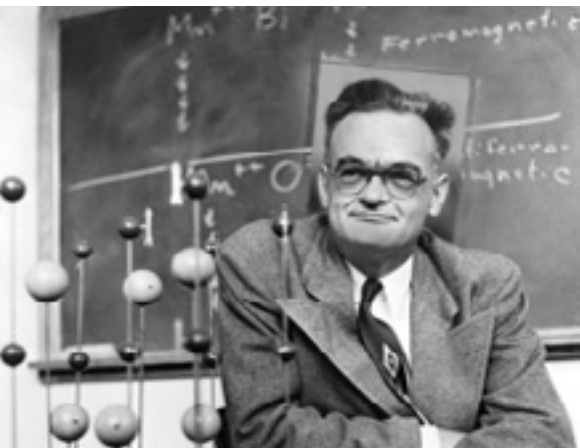
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At Carnegie Mellon, Zener used geometric programming and his affinity for thermodynamics to show that it should be possible to generate electricity, at an acceptable cost and without air pollution, from the temperature difference between warm ocean-surface water and cold deep water. Demonstration of the feasibility of this idea requires a large engineering effort that only the Japanese have been willing to fund. Other countries have chosen to invest in wind and solar energy as alternatives to fossil fuels. Regardless of its fate, however, "ocean thermal" is an example of the daring originality of a unique mind.

Zener was a humble, scrupulously honest, and enthusiastic physicist with a keen sense of how his talents could be most effectively used, and he was generous in his credits to those who tested or worked to develop his ideas. He was generous as well with his time in counseling students and advising government agencies, and he respected all persons with whom he worked. Zener's policy was never to discuss ideas he was researching, as he did not want to prevent someone else from exploring the same or related topics. Using skills rarely combined in one person, he pioneered the building of bridges between physics, materials science, and engineering—an interdisciplinary approach now recognized as materials engineering.

REFERENCES

Anonymous. 2013. Clarence Zener. In *Wikipedia*. Online at *en.wikipedia.org/wiki/Clarence_Zener*, accessed on December 24, 2013.

Hoddeson, L. 1981. Interview with Dr. Clarence Zener in his office at Carnegie Mellon University. American Institute of Physics, College Park, MD. Online at *www.aip.org/history/ ohilist/4996.html*, accessed on December 24, 2013.

Maguire, M. 1985. Clarence Zener a rare, strange genius. *Carnegie Mellon Magazine* Winter:18–19.

Saxon, W. 1993. Clarence Zener, 87, physicist and professor at Carnegie Mellon. *New York Times*, July 6, B6.

SELECTED BIBLIOGRAPHY

1931 Low-velocity inelastic collisions. *Phys. Rev.* 38:227–281.

1932 Non-adiabatic crossing of energy levels. *Proc. Roy. Soc.* (London) A137:696–702.

1934 A theory of the electrical breakdown of solid dielectrics. *Proc. Roy. Soc.* (London) A145:523–529.

1939 A method of calculating energy losses during impact. *ASME J. of Appl. Mech.* 6:A67–A70.

1940 Internal friction in solids. *Proc. Roy. Soc.* (London) 52:152–156.

1941 Theory of internal friction introduced by cold working. *Phys. Rev.* 60:455–457.

Theory of the elasticity of polycrystals with viscous grain boundaries. *Phys. Rev.* 60:906–908.

1944 With J. H. Hollomon. Plastic flow and rupture of metals. *Trans. ASM* 33:163–215.

1945 The fracture stress of steel. *Rev. Mod. Phys.* 17:20–26.

1946 Kinetics of decomposition of austenite. *Trans. AIME* 167:550–595.

A theoretical criterion for the initiation of slip bands. *Phys. Rev.* 69:128–129.

1947 Stress-induced preferential orientation of pairs of solute atoms in metallic solid solution. *Phys. Rev.* 71:34–38.

1948 *Elasticity and anelasticity of metals.* Chicago: University of Chicago Press.

1949 Relaxation phenomena in metals. *Physica* 4:111–118.

Theory of growth of spherical precipitates from solid solution. *J. Appl. Phys.* 20:950–953.

1950 The role of statistical mechanics in physical metallurgy. In *Thermodynamics in Physical Metallurgy.* pp. 16-27. Cleveland, OH: ASM.

Ring diffusion in metals. *Acta Cryst.* 3:346–354.

1951 Interaction between the d-shells in the transition metals: II. Ferromagnetic compounds of manganese with perovskite structure. *Phys. Rev.* 82:403–405.

1955 Impact of magnetism upon metallurgy. *Trans. AIME* 203:619–630.