

## IN MEMORIAM

### Michell J. Sienko

Michell J. Sienko was born on May 15th, 1923, in Bloomfield, New Jersey. After a distinguished undergraduate career at Cornell University, he immediately went to the University of California, Berkeley, to study for a Ph.D. under the direction of Professors W. M. Latimer and E. D. Eastman. At Berkeley he was committed to full-time research for the Manhattan project, and earned his Ph.D. in February 1946 on the high-temperature thermodynamics of molten salts in the near-record time of little more than two and one-half years. From 1946 to 1947 he worked with Professor R. A. Ogg, Jr., at Stanford University, most of which time was spent in unsuccessful attempts to repeat those famous experiments in which "superconductivity was discovered" in quenched sodium-ammonia solutions. Toward the end of this postdoctoral period, Sienko received a telegraphed invitation from Professor P. J. W. Debye, then Chairman of the Chemistry Department at Cornell, who offered him the position of instructor and the chance to teach freshman chemistry—a challenge which he could not resist.

As Sienko himself put it, "I entered the academic marketplace at the bottom of the ladder at Cornell." Although charged with heavy teaching responsibilities (freshman chemistry, classes of up to 1200 students) he set up a research program to investigate the physical properties of metal-ammonia solutions. With his students, he studied phase separation, conductivity, salt effects, surface tension, and the Metal-NonMetal

transition. Then a chance visit to Cornell by Dr. E. O. Brimm of Linde corporation sparked Sienko's (latent) interest in the solid state. As Sienko recalled, "[Dr. Brimm] set on my desk two samples, one blue and the other bronze, of what he called 'tungsten bronzes'. It immediately struck me that these solid-state compounds, which were (then) considered to be mixtures of pentavalent and hexavalent tungsten, were actually analogs of the sodium-ammonia solutions—except that the sodium was now dissolved in a solid-state matrix." Thus, the scene was set for three decades of Sienko's involvement and example in solid-state chemistry. Following this scientifically reasoned hunch, he and his group made a systematic study of the electric, magnetic, and magnetic-resonance properties of the bronzes, uncovering on the way several new nonstoichiometric compounds, and a new important general principle; viz., oxygen removal from a transition-metal oxide framework has a one-to-one correspondence to (donor) metal insertion. Furthermore, using Sir Nevill Mott's revolutionary ideas of the Metal-Nonmetal transition in condensed phases, Sienko predicted and found such a transition, not only in the tungsten and vanadium bronzes, but also in oxygen-deficient analogs.

Thus, in 1963 he laid the foundation of the modern picture of electron transport in the nonstoichiometric transition-metal oxide bronzes. These embryonic ideas were then extended and developed by John B. Goodenough to give the present model of

electronic structure that underlies most solid-state transition-metal oxide studies. Similarly, his sustained interest in metal–ammonia solutions paid rich dividends. Once again in 1963, whilst heavily immersed in the transition-metal oxide work, Sienko was invited by Professor Gerard Lepoutre to present a plenary lecture at the first Colloque Weyl, held in Lille, France. Working from data from some unpublished theses, including his own students' work, and under the valuable stimulus of his Cornell colleague and friend Professor Ben Widom, Sienko was led to the startling discovery that the liquid–liquid coexistence curves for Li–NH<sub>3</sub>, Na–NH<sub>3</sub>, and K–NH<sub>3</sub> solutions were almost unique in exhibiting parabolic dependencies, whereas all other critical phenomena (and, indeed, the best theoretical models) correspond to cubic coexistence curves. Sienko suggested that the unique character of the metal–ammonia coexistence curve was due to extremely long-range electronic interactions in these solutions. It is interesting to record here the link between Sienko's insightful suggestions and certain of the comments made by Professor Ogg in 1946 concerning the possibility of high-temperature superconductivity in metal–ammonia solutions. Once again, Sienko's "global" reasoning led him to show in 1963 that this remarkable liquid–liquid phase separation in metal–ammonia solution was intimately related to the Metal–NonMetal transition in these systems. Subsequently, with this writer in 1978 and 1981, he suggested that the Mott description of the Metal–NonMetal transition had certain universal features in prescribing both the electronic and thermodynamic facets of the transition in condensed phases.

From the mid-1960s, Sienko's research interests broadened still further; his solid-state contributions (in addition to his commitment to his beloved bronzes) centered on three kinds of materials: the layer-type transition-metal dichalcogenides, metal-

atom cluster compounds of the Chevrel type, and "expanded-metal" compounds based on frozen solutions of alkali metals in liquid ammonia.

The impact of his research in these varied areas was equally important. In his work on Chevrel phases and the layered compounds he elegantly demonstrated how superconductivity and related phenomena can be influenced profoundly by chemical structure, stoichiometry, and bonding. In a different area, Sienko and his collaborators were able to demonstrate that the exotic low-temperature compounds Li(NH<sub>3</sub>)<sub>4</sub> and Ca(NH<sub>3</sub>)<sub>6</sub> represent unique "expanded metals," just on the metallic side of the Metal–NonMetal transition. His most recent discovery, Li(CH<sub>3</sub>NH<sub>2</sub>)<sub>4</sub>, appears to be the first example of the elusive paired-electron state right at the Metal–NonMetal transition.

With this brief summary, I have tried to capture something of the extraordinary depth and variety of Mike Sienko's spectrum of research interests; his research encompassed all aspects of condensed phase chemistry associated with the transition from localized to itinerant electron behavior. In all areas, Sienko's special flair was the pragmatic combination of scientifically reasoned hunches, backed up by skillful synthesis and precise characterization of advanced materials. This writer suggests that this particular confluence of research talents derived from the inspiration given by Professor J. L. Hildebrand at Berkeley during Sienko's Ph.D. tenure. In essence, Sienko's contribution can be recorded in terms of bringing a chemist's view to a physical problem; in his own words:

"... it will probably be the inorganic chemists who will contribute most to solving these problems, since solid-state physicists are generally reluctant to tackle chemicals more complex than one-component systems and physical chemists do not have the advantage of the Periodic Table."

*From "The Alkali Metals" (Special Publication No. 22), Chem. Soc., London, 1967*

In this manner he contributed significantly to unraveling the chemistry and physics at the Metal–NonMetal transition.

Mike Sienko was a leading figure in the solid-state community, not only for his pioneering research on important materials, but also because he unselfishly served the community as Editor of the *Journal of Solid State Chemistry* from 1969 to 1982. In the thirteen eventful years he was editor of this international journal, he prompted, catalyzed, and helped advance the development of solid-state chemistry in the United States to its present position.

Similarly, Mike's contribution to chemical education must be judged as being truly outstanding. In addition to his inspirational teaching of over 30,000 undergraduate students and some 40 graduate students at Cornell, the most visible impact that Mike made upon chemical education was through his published books coauthored with Professor R. A. Plane. "Sienko and Plane" is probably the most famous—and, integrated over its lifetime, is surely the most influential—introductory chemistry text ever written. It has had more influence on the teaching of chemistry throughout the world than any other written work. The overdue recognition of Mike Sienko's 30 years of outstanding excellence and commitment to teaching came in 1983 when he received the American Chemical Society Award in Chemical Education.

In summary, here was a man who was a great scientist as well as one of the guiding lights in the evolution of modern chemical education in the United States and throughout the world.

Finally, we will not forget his most engaging personality and endearing human qualities. Each of us will carry his or her own affectionate recollections of Mike's warmth, hospitality and friendliness; I have chosen a short quotation from Mike's own writing which perhaps summarizes something of his approach to his fellow man:

. . . no goal is worth pursuing if it means that human qualities are destroyed. Respect for one's fellowman comes first.

from "Who's Who in America," 41st ed.,  
1980–1981, Vol. 2

Michell J. Sienko died peacefully, after a brief illness, on the 4th December 1983. The scientific world has lost a dear friend and colleague.

P. P. EDWARDS  
*Guest Editor*

### HONORS AND GUEST APPOINTMENTS

Fulbright Lecturer, Université de Toulouse (1956–1957); Visiting Professor, American College in Paris (1963–1964); Guggenheim Fellow, CNRS Rayons X, Grenoble (1970–1971); Gastprofessor, Institut für Physikalische Chemie, University of Vienna (1974–1975); Visiting Fellow, Clare Hall, Cambridge University (1978–1979); Visiting Professor, University of Grenoble (Summer 1980).

### AWARDS AND RECOGNITIONS

College of Engineering at Cornell, First Sporn Award for Excellence in Teaching; Clark Distinguished Teaching Award; Member of Examination Committee of the American Chemical Society Division of Chemical Education, Chairman of the Inorganic Subcommittee; American Chemical Society Award in Chemical Education.

National Aeronautics and Space Administration Lecturer at Washington State University, Francis Clifford Phillips Lecturer at the University of Pittsburgh, Byron Regal Lecturer at Northwestern University.

Editor, *Journal of Solid State Chemistry*. Member, Solid State Sciences Committee of the National Academy of Sciences (Basic Science Panel).

**RESEARCH COLLABORATORS****Graduate Students**

E. Bell (1984)	J. Gavis (1953)	D. Kudrak (1966)	J. Sohn (1965)
J. M. Berak (1969)	J. Gendell (1961)	P. Lambert (1985)	A. M. Stacy (1981)
G. H. Bouchard (1968)	W. S. Glaunsinger (1972)	C. McEwen (1983)	R. A. Stairs (1955)
J. R. Buntaine (1979)	J. Gulick (1969)	S. M. Morehouse (1962)*	J. F. Thomas (1973)
A. Chang (1978)	D. Hodul (1978)	C. Page (1984)	T. B. N. Truong (1960)*
P. Chieux (1970)	F. Holly (1962)	H. Perkins (1965)	D. R. Wanlass (1973)
L. E. Conroy (1955)	D. Huntley (1983)	J. H. Perlstein (1967)	P. F. Weller (1962)
B. L. Crowder (1963)	S. Issler (1985)	T. David Pfeuty (1973)	J. E. Young (1971)
F. S. Delk (1979)	D. C. Johnson (1983)	J. B. Russell (1956)	
E. Dolan (1963)	J. Kernahan (1953)*	D. St. Julien (1984)	
W. G. Fisher (1978)	F. Kupka (1952)*	L. F. Schneemeyer (1978)	

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\* M. S. students.

**Postdoctoral and Visiting Scientists**

B. Banerjee (1961)	P. P. Edwards (1977)	J. L. Krause (1972)	J. K. Petersen (1976)
M. Bayard (1976)	R. Hagendorn (1980)	A. Lesaicherre (1963)	J. Pivnichny (1973)
B. Y. Brutch (1966)	M. R. Harrison (1983)	A. R. Lulis (1977)	J. L. Ragle (1962)
B. K. Chakraverty (1978)	R. Hemmel (1979)	N. Mammano (1968)	A. F. Reid (1967)
N. Chevreau (1984)	K. Hiebl (1979)	B. R. Mazumder (1960)	P. Rogl (1979)
P. Courtine (1970)	F. Hubble (1973)	B. F. Mentzen (1975)	R. J. Sobczak (1977)
P. Damay (1974)	J. F. Hunt (1973)	P. Molinie (1978)	J.-M. Tarascon (1982)
P. G. Dickens (1972)	H. Kessler (1969)	H. Oesterreicher (1968)	S. Zolotov (1972)