Scientific Beginnings – From Low-Temperature Physics and Chemistry to Hyperfine Interactions

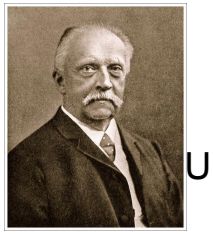
Early work of David A. Shirley and his group

David Shirley was born in 1934 in North Conway, New Hampshire.
After finishing school, he studied chemistry at the University of Maine, Augusta.
He obtained the B.S. in chemistry there in 1955 and went to Berkeley to begin doctoral work.
In Berkeley, he joined the research group of Prof. W.F. Giauque, director of the Low Temperature Laboratory…

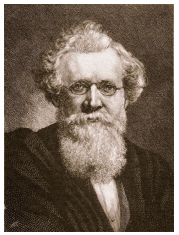
Outline

- I. Scientific beginnings – Antecedants, 1955-59.
- II. Independent work – The years of rapid development, 1959-64.
- III. Consolidation and growth; the rise and fall of Hyperfine Interactions, 1965-75.

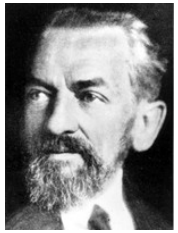
I. Antecedents



Hermann von Helmholtz
(1821-1894)
Univ. Berlin, PTR



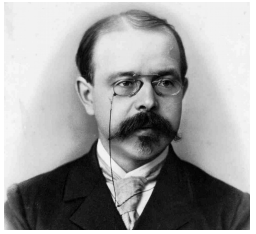
August Wilhelm von Hofmann
(1818-1892)
Univ. Berlin



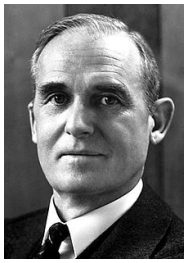
Otto Lummer
(1860-1925)
Univ. Berlin, 1894

Richard Abegg
(1869-1910)
Univ. Berlin, 1891

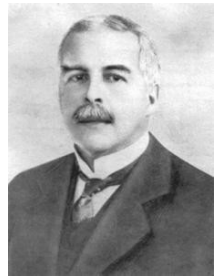
Walther Nernst
(1864-1941)
Göttingen, Berlin



George Ernest Gibson
(1884-1959)
Univ.Breslau, 1911



Gilbert Newton Lewis
(1875-1946)
UC Berkeley



William Francis Giauque
(1895-1982)
UC Berkeley, 1922

David A. Shirley
UC Berkeley, 1959

Thesis work 1955-59

The entropy of iodine. Heat capacity from 13 to 327°K. Heat of sublimation.
Shirley, D. A.; Giauque, W. F.
J. Am. Chem. Soc., vol. **81**, pp. 4778-4779, 1959

The Heat Capacity of Lithium Chloride from 15 to 325 Degrees Kelvin
D.A. Shirley
J. Am. Chem. Soc., vol. **82**, no. 15, pp. 3841-3843, 1960

Even before his PhD degree was granted in 1959, David Shirley took a position on the staff of the 'Rad Lab' in 1958 and began setting up to do ***nuclear orientation*** experiments. His experience with cryogenics and the availability of many radioactive isotopes at the lab were a perfect combination for exploiting this relatively new technique to obtain nuclear physics (and later solid-state) information.

The laboratory changed its name to 'Lawrence Radiation Laboratory' after the early death of E.O. Lawrence in 1958, and Edwin Mc Millan became its second director.

David Shirley took a joint position as assistent professor in the UC Chemistry Department in 1960 and established his own research group in the Nuclear Chemistry Division of LRL.

Brief intermezzo: A quick quide to nuclear orientation

Nuclear orientation (NO) refers generically to an ensemble of atomic nuclei whose directions in space (i.e. their nuclear spin axes) are not *isotropic* – they do not exhibit spherical symmetry. One method is *low-temperature thermal-equilibrium* NO.

If *radioactive nuclei* are used, their orientation can be detected sensitively by observing the angular distribution of the radiations they emit.

This method of NO requires fulfillment of three experimental conditions:

i. Specification of a *quantization axis* or preferred direction in space. This is usually an axis of crystalline symmetry of the host material, or an applied field.
ii. Production of an *energy splitting* ΔE between the nuclear substates relative to the quantization axis. This can be through interaction of nuclear electromagnetic moments with their surroundings (***hyperfine interactions***), or a direct nuclear Zeeman splitting.
iii. Lowering the *temperature* of the sample until $kT \approx \Delta E$, typically around 10 mK. This can be experimentally challenging. The earliest methods (Pound, Rose, Gorter, Bleaney) used paramagnetic crystals as hosts, which were cooled directly by adiabatic demagnetization – *host material* and *cooling agent* are identical.

II. Years of rapid growth

Publications, 1960-61

Nuclear Orientation of Iodine by Electric hfs Alignment: C. Johnson, J. Schooley, D.A. Shirley, Physical Review, vol. 120, no. 5, pp. 1777-1780, 1960

Nuclear Orientation of Tb-160: C. Johnson, J. Schooley, D.A. Shirley, Physical Review, vol. 120, no. 6, pp. 2108-2113, 1960

Nuclear Moment of Ce-137m by Nuclear Alignment: J. Haag, C.E. Johnson, D.A. Shirley, D. Templeton, Physical Review, vol. 121, no. 2, pp. 591-594, 1961

γ-Ray Anisotropies from Oriented Pm-144: D.A. Shirley, J.F. Schooley, J.O. Rasmussen, Physical Review, vol. 121, no. 2, pp. 558-561, 1961

Nuclear Orientation of Paramagnetic Impurity Ions: Morton Kaplan and D. A. Shirley, Physical Review Letters, vol. 6, 361, 1961

Nuclear Orientation of Dy-155 and Dy-157: Quirino Navarro and D. A. Shirley, Physical Review, vol. 123, no. 1, pp. 186-189, 1961

Recoil-Free Resonant Absorption in Au-197: *D.A. Shirley, M. Kaplan, P. Axel, Physical Review, vol. 123, no. 3, pp. 816-830, 1961*

Nuclear Orientation of Pm-143: C. A. Lovejoy, J. O. Rasmussen, D. A. Shirley, Physical Review, vol. 123, pp. 954-956, 1961

Nuclear Orientation of Nd-147: G. Westenbarger and D.A. Shirley, Physical Review, vol. 123, no. 5, pp. 1812-1818, 1961

Interpretation of the Isomeric Chemical Shifts in Au-197: *D.A. Shirley, Physical Review, vol. 124, no. 2, pp. 354-358, 1961*

Paramagnetic Resonance of Trivalent 147-Pm in Lanthanum Ethylsulfate: *H.J.Stapleton, C.D. Jeffries and D.A. Shirley, Physical Review, vol. 124, no. 5, pp. 1455-1457, 1961*

Launch of the Shirley research group, diversification: 1960-64

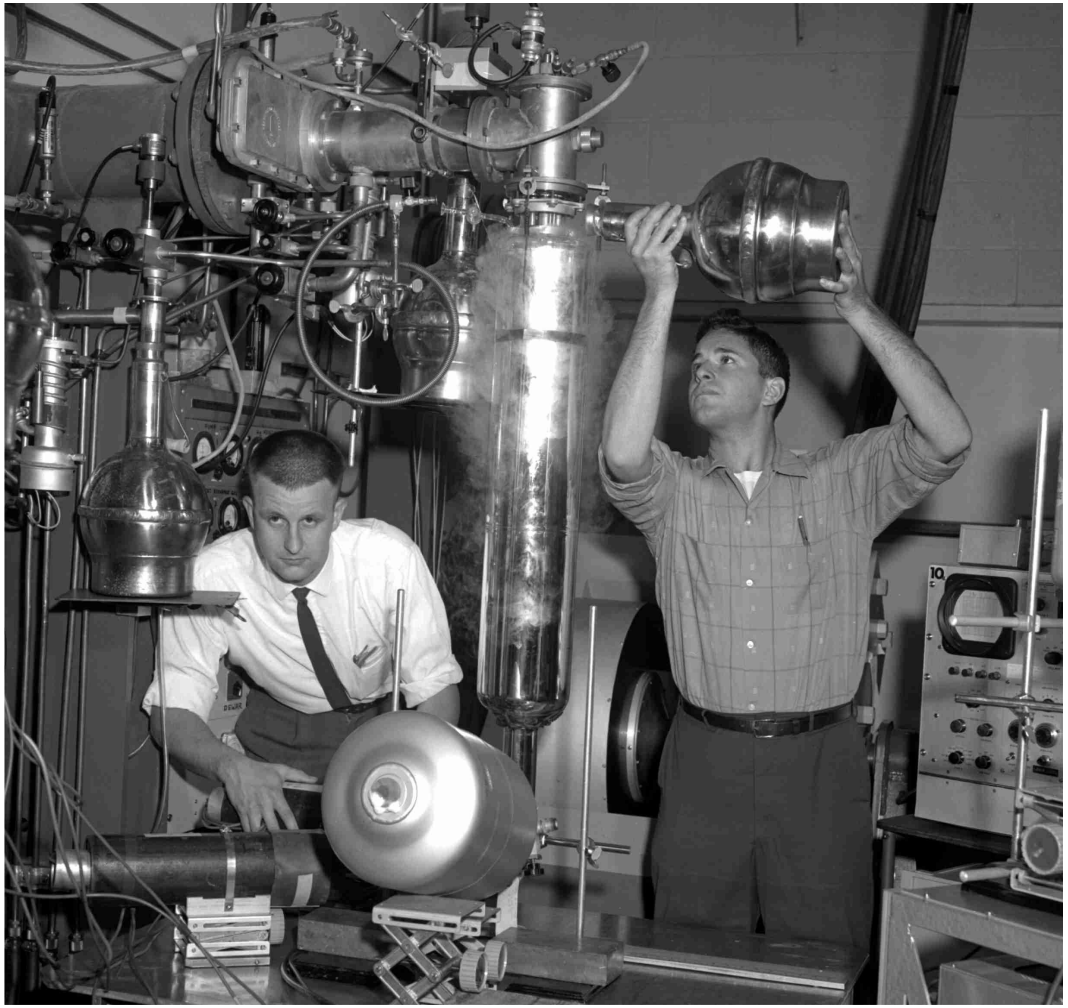
David Shirley's *first collaborators* were other postdocs and young visitors to the lab, or else staff and faculty members: Charles Johnson, Jim Schooley, Morton Kaplan; and John O. Rasmussen, David Templeton, Carson D. Jeffries, B.R. Judd…

After 1960, he had his own graduate students: Quirino Navarro, Ronald W. Grant, C.A. Lovejoy, Gene Westenbarger, Johan Blok, Richard Levy, Richard Frankel, D.A. Keller, Hollis Wickman…

Nuclear orientation (NO) in paramagnetic crystals was quickly complemented by other modern techniques: The 'universal method' of NO using ferromagnetic metal hosts, observation of particle emissions (alpha and beta particles, conversion electrons), the use of Ge(Li) semiconductor γ-ray detectors; as well as completely new methods (Mössbauer effect, ESR, perturbed γ-γ angular correlations (PAC))… – More about PAC from Heinz Haas in the following talk.

Visitors from other laboratories joined the group, sometimes for longer periods: Eckart Matthias from Uppsala, 1963-69 (PAC); Nick Stone from Oxford, 1963-64 (NO); Stig Hagström from Uppsala, 1965-66 (photoelectron spectroscopy)…

1962-64



David Shirley in 1964, setting up a nuclear orientation experiment with his graduate student Richard Frankel.

The sample is in the glass Dewar in the center, which contains a pumped liquid He bath to produce the 1 K initial temperature. The large magnet in the background can be rolled up as required. The counting table in lower foreground holds γ-ray detectors (Na(Tl)I and Ge(Li)).

New Perspectives – 1964

In 1964, David Shirley was 30 years old. He was promoted to Associate Professor in the Dept. of Chemistry, UC Berkeley.

His research group was now large and international, known for innovative work.

Around this time, he began work with photoelectron spectroscopy, using a converted spectrometer in the Field-Free Laboratory with the cooperation of Jack Hollander. A graduate student, Charles S. Fadley, was assigned to this project, and a visitor from Uppsala, Stig M.B. Hagström, lent his expertise.

This field over the next 10 years would overtake and supplant the hyperfine interactions work which dominated the activities of the group in the mid-1960's.
– More about these developments in the talk by Chuck Fadley.

In a few years, David Shirley had gone from being a graduate student working in classical physical chemistry with chemical-thermodynamic methods from a long tradition – to being the leader of a successful research group dealing with a broad spectrum of problems in nuclear and solid-state physics, metrology and fundamental physics; and to being a tenured professor at a major university, with increasing responsibilities in teaching and administration.

III. Consolidation and growth — 1965-75.

"The rise and fall of Hyperfine Interactions"

During the 10-year period from 1965 to 1975, the Shirley group enjoyed a strong international reputation and attracted visiting scientists from many places. We can mention only a few highlights here.

The group published around 10 articles/year in refereed journals from 1965-71, then around 18/year from 1972 onwards. The jump was due to the high productivity of XPS, which predominated over HFI after 1971. We concentrate here on the latter.

Some important developments included:

- The combination of the sensitivity of excited-nuclear methods with the precision of magnetic resonance (PAC/NMR [1966], NO/NMR [1966/67]);
- Organizing the Asilomar Conference on "*Hyperfine Structure and Nuclear Radiations*" (E. Matthias, D.A. Shirley, August 1967) and the associated book, perhaps the high point of HFI research in the group;
- The introduction of modern technology (superconducting magnets, dilution refrigerators, Ge(Li) γ-ray detectors, fast electronics…

Magnetic Resonance with Excited Nuclei

The excited-nuclear methods for investigating hyperfine interactions are very sensitive, since they detect nuclear radiations that can be counted with great efficiency. On the other hand, they may have limited precision (particularly NO, an integral method; PAC and Mössbauer Effect are intrinsically spectroscopic methods with high resolution).

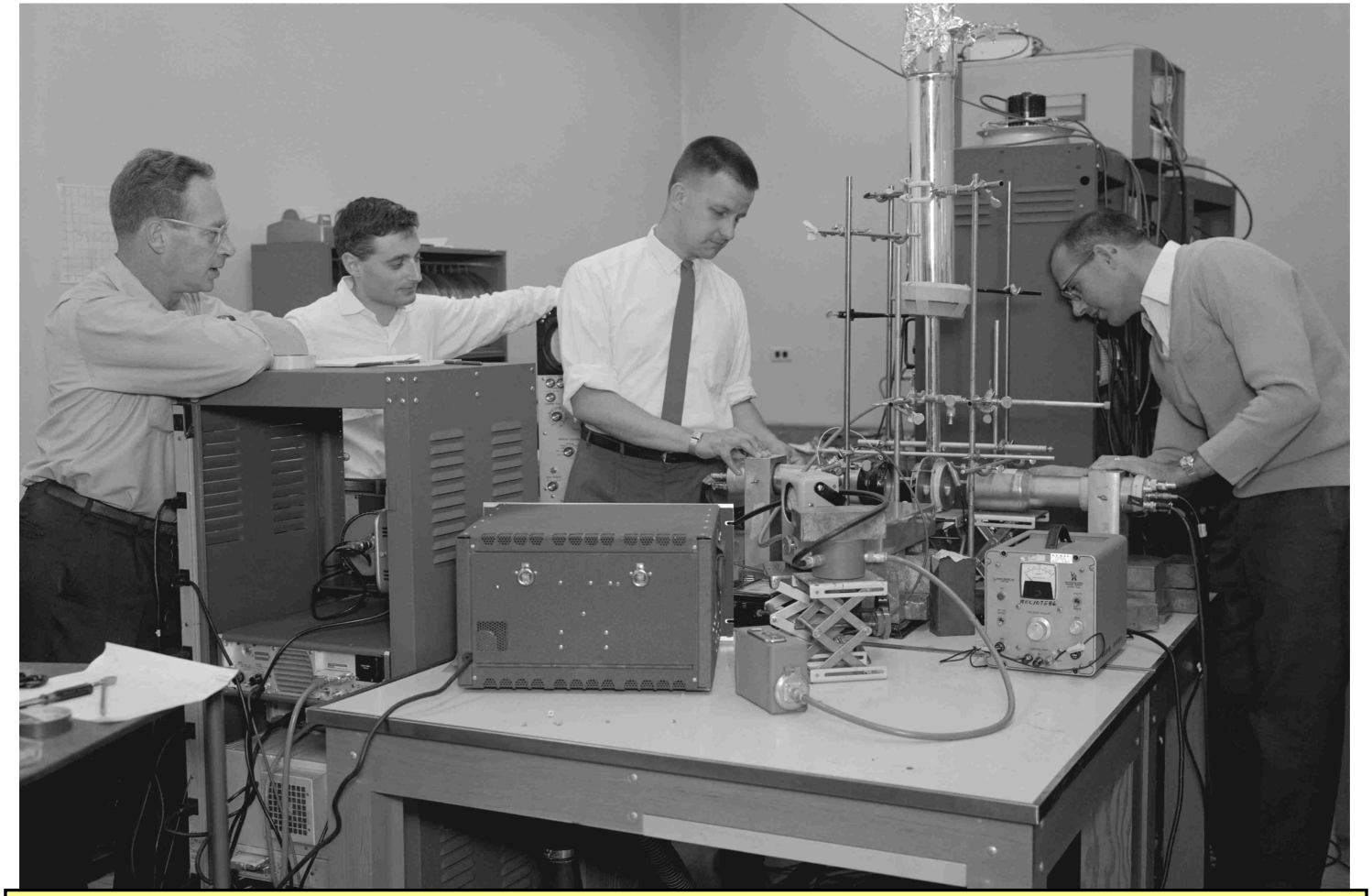
Combining excited-nuclear methods with nuclear magnetic resonance (NMR) potentially provides the advantages of both techniques. This was first demonstrated by a team from the Shirley group, who combined PAC and NMR:

VOLUME 16, NUMBER 22 PHYSICAL REVIEW LETTERS 30 MAY 1966

DETECTION OF NUCLEAR MAGNETIC RESONANCE IN A 235-nsec NUCLEAR STATE BY PERTURBED ANGULAR CORRELATIONS

E. Matthias, D. A. Shirley, M. P. Klein, and N. Edelstein
Lawrence Radiation Laboratory, Department of Chemistry and Laboratory of Chemical Biodynamics, University of California, Berkeley, California
(Received 25 April 1966)

(Parallel development of methods using nuclear reactions or Stern-Gerlach selection followed by NMR of beta-active nuclei occurred at several places beginning in 1959.)



The team that introduced PAC/NMR. *From left*: Melvin P. Klein of CBL, later often a visitor in Berlin; Norman Edelstein of LRL (the two resonance experts). *Center, right:* David Shirley and Eckart Matthias of the Shirley group (the excited-nuclear specialists). Early **1966**.

Nuclear Orientation – NMR

This most useful combination was demonstrated by Eckart Matthias and graduate student Jim Holliday in summer 1966, while David Shirley was on sabbatical with an NSF Fellowship at the Clarendon Laboratory, Oxford.

PHYSICAL REVIEW
LETTERS

VOLUME 17 — 24 OCTOBER 1966 — NUMBER 17

NUCLEAR MAGNETIC RESONANCE IN POLARIZED NUCLEI*

E. Matthias and R. J. Holliday
Lawrence Radiation Laboratory, University of California, Berkeley, California
(Received 26 September 1966)

It was quickly recognized by David Shirley and a graduate student at Oxford, James E. Templeton, that the small signals seen by Matthias and Holliday were due to the wide NMR lines in the ferromagnetic host; they improved the method by using frequency modulation to match the rf bandwidth to the NMR linewidth. They demonstrated the results with both γ-rays and β-particles from ^{60}Co*Fe.*

David Shirley was promoted to full professor at UC Berkeley in 1967.

VOLUME 18, NUMBER 7 PHYSICAL REVIEW LETTERS 13 FEBRUARY 1967

RESONANT DESTRUCTION OF NUCLEAR ORIENTATION IN FERROMAGNETS*

J. E. Templeton and D. A. Shirley†
The Clarendon Laboratory, Mullard Cryomagnetic Laboratory, Oxford, England
(Received 22 December 1966)

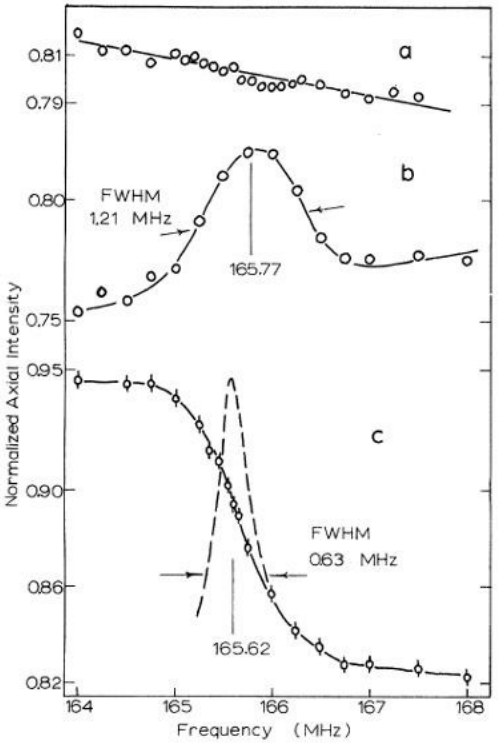


FIG. 1. Line shapes for Co^{60} in iron, obtained by sweeping with methods (a)-(c) described in text. For these curves H_1 was approximately 3, 4, 5, and 3 mg, respectively.

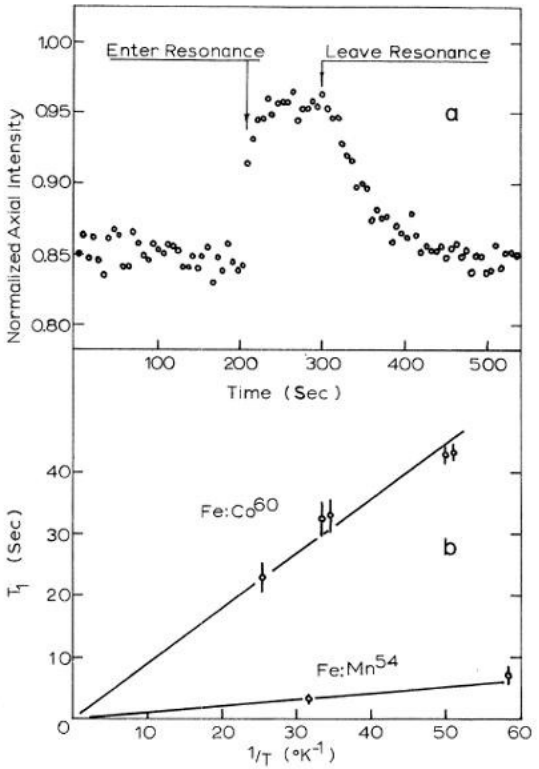
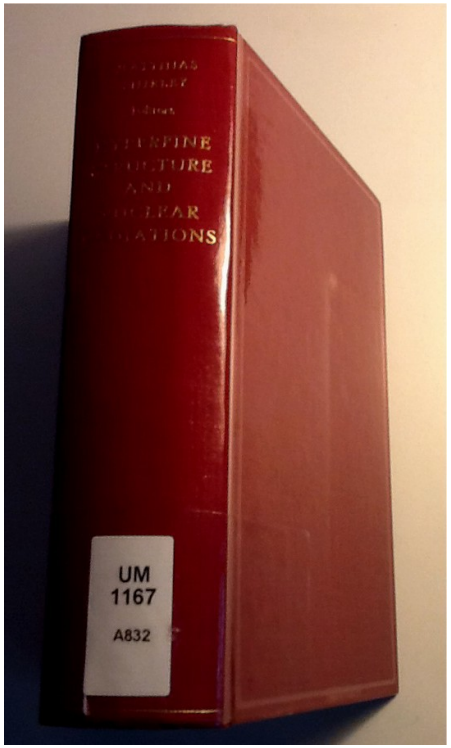


FIG. 2. Relaxation effects. (a) Destruction and recovery of Co^{60} orientation on entering and leaving resonant region with constant amplitude H_1 of 3 mg. (b) T_1 vs $1/T$ for the two alloys.

The Asilomar Conference on Hyperfine Interactions – 1967

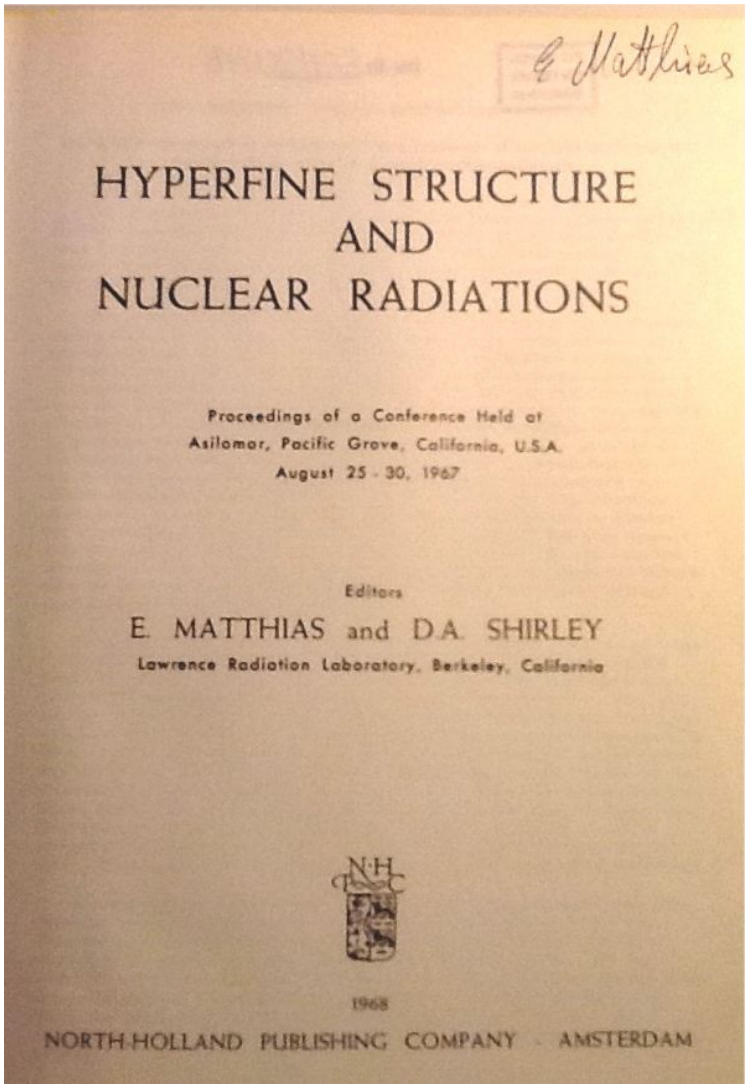
This conference, organized by Eckart Matthias and David Shirley shortly after the latter's return from Oxford, took place at the Asilomar Conference Grounds in Central California in August, 1967. It was the first in a long series of conferences (the 17th is planned for September, 2014 in Canberra, with a slightly different name).



It brought together around 175 researchers from 15 countries in the field of hyperfine interactions with excited nuclei, and firmly established the Shirley group as a leader in that field. The accompanying prodeedings volume, along with the one from a NATO Summer School the previous year, organized by Arthur J. Freeman and Richard B. Frankel, a Shirley alumnus, served as a useful source of information for some years to come.

The Asilomar Conference

The meeting hall at Asilomar

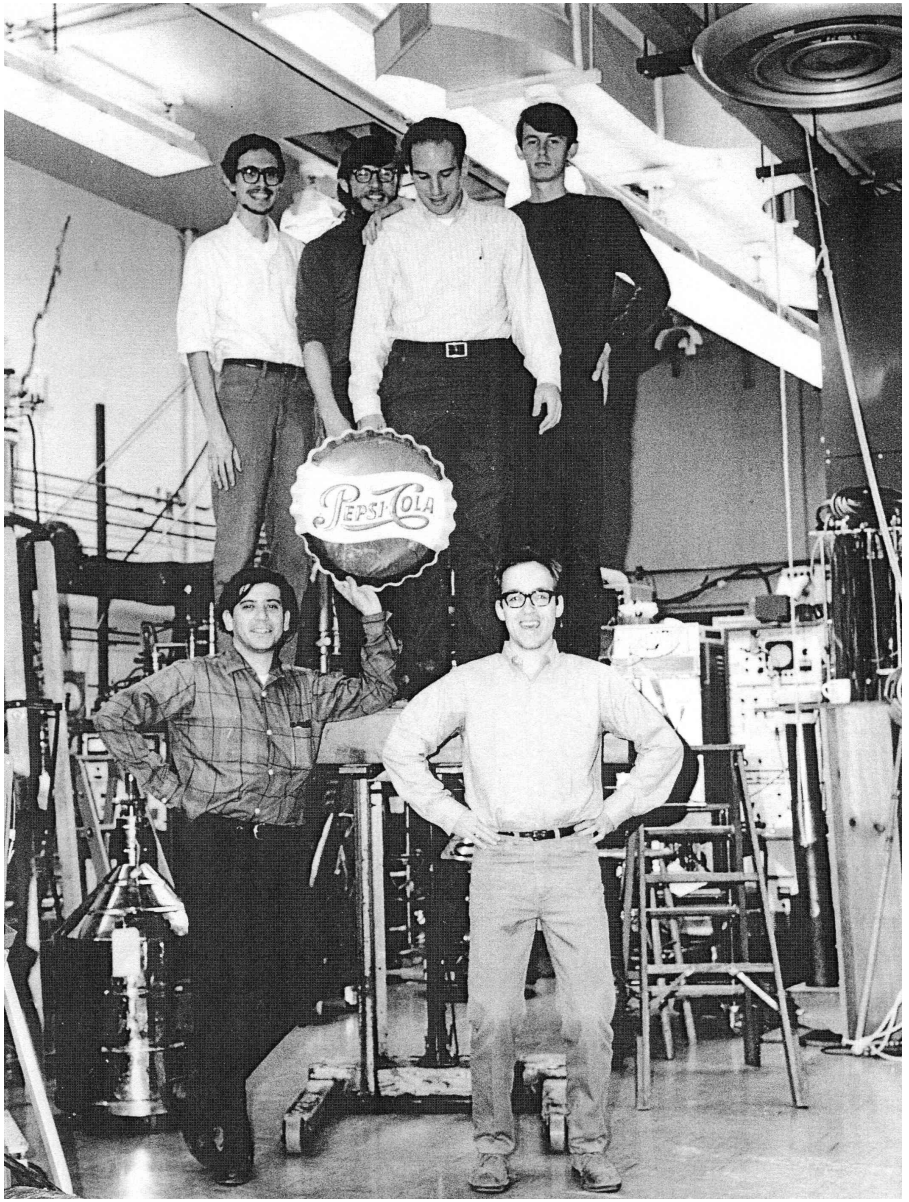


Frontispiece of the proceedings

The Shirley Group in 1969

Some of the graduate students in the lab in the Nuclear Chemistry building.

Front, standing: Dan Salomon, Gus Apai;
Above: Bill Brewer, Chuck Fadley, Roger Pollak, Rick Streeter



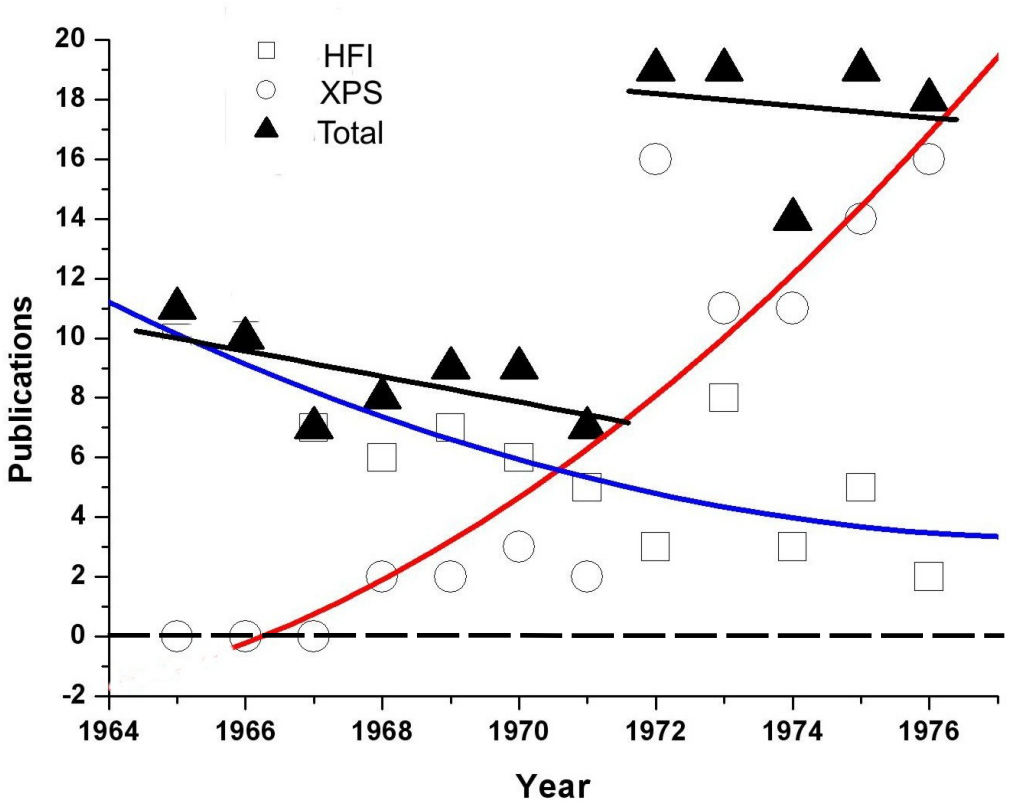
The Shirley Group in 1969

Students, staff, visitors... *1st row*: Günter Kaindl, Norman Edelstein, Dan Salomon, Roger Pollak.

Above and behind: Tom Koster, Rick Streeter, Wini Heppler, Art Soinski, Gus Apai, Dr. Phillips, Bill Brewer, Fred Bacon, Sammy Hung, Dorothy Chan.

The transition from Hyperfine Interactions to Photoelectron Spectroscopy

The decline of HFI, reflected in publication rate



As mentioned, the research emphasis in the Shirley group changed over the decade 1965-1975, perhaps in part because its HFI research was mainly in the domain of physics, while the group was anchored in physical chemistry at UC Berkeley.

Aditionally, XPS was a growing and exciting field which initially required a less demanding technology (but soon led to Big Science…).

David A. Shirley and the *Fachbereich Physik, Freie Universität Berlin*

Around the time of the Asilomar Conference, *Eckart Matthias*, then a staff scientist at LRL and a member of the Shirley group, was approached with the possibility of becoming director of the *I. Physikalisches Institut* at the *Freie Universität* in Berlin, as successor to its founding professor, Hans Lassen, who had retired in 1965.

To pursue this possibility, he spent the 1967-68 academic year at the TU München in the group of R.L. Mössbauer, where he completed his *Habilitation*, a prerequisite for the position in Berlin. He returned to Berkeley, having made many new contacts in Germany, and arranged for several visiting scientists to join the Shirley group. In the fall of 1969, he took up his new position as professor in Berlin.

The *I. Physikalisches Institut* was combined with the other physics institutes during the University Reform in 1972 to form the *Fachbereich Physik*, which still bears this name.

Numerous contacts, scientific visits and collaborations in both directions as well as the scientific influence of David Shirley on the development of the *FB Physik* led to a strong connection over the years, which was recognized by conferring the first honorary doctorate from the *FB Physik* on David Shirley in 1987.

Members of the Shirley group and *FU Physik*

Many visiting scientists in the Shirley group were later associated with the *FB Physik*:

Eckart Matthias, Miller Fellow and Staff Scientist at LRL, later professor at FU;
Dieter Quitmann, at LRL 1967-69, later professor at FU;
Helmut Gabriel, at LRL 1967-69, later professor at FU;
Erwin Klein, at LRL 1968-69, later professor at FU;
Günter Kaindl, Miller Fellow 1969-72 and visiting scientist at LRL, later professor at FU;
Heinz Haas, LRL 1968-70, later *Privatdozent* at *FU-Physik*;
Heinz-Eberhard Mahnke, LRL 1970-72, later *Privatdozent* and *Honorarprofessor* at FU;
Herbert Rinneberg, LRL 1971-73, later *Privatdozent* at *FU-Physik*.

In addition, several graduate students of the Shirley group were later at *FU-Physik*:

James Huntzicker, PhD 1968, postdoc at FU 1969-71;
Steven Rosenblum, PhD 1969, postdoc at FU 1970-72;
William Brewer, PhD 1970, NSF Fellow at FU, 1970; later professor at FU;
Dan Salomon, PhD 1971, postdoc at FU 1974-76.

David Shirley spent a semester at the *FU-Physik* as an NSF Fellow in 1970, and more tban a year as *A.v.Humboldt* Fellow in 1989-90.
A number of other scientific exchanges (sabbaticals etc.) took place, especially from the mid-1970s to the early 90s.

Christmas in Berlin, 1970, at the house of Helmut Gabriel (seated, right). Essentially everyone in the picture had spent time at Berkeley and was now associated with the *FU-Physik*. David Shirley is seated in the center.

Other scientific collaborators of the Shirley group, 1965-75

Of course there were many scientific visitors and collaboration partners of the Shirley group in the years 1965-75 who were ***not*** later connected to the *FB Physik*. They also deserve mention, although this list cannot claim to be complete:

Nicholas J. Stone, 1963-64; Clarendon Laboratory, Oxford University
Stig B. Hagström, 1965-66; Uppsala, later Linköping, Xerox PARC, Stanford
Israel Nowik, 1964,65; Hebrew University, Jerusalem
James E. Templeton, 1967-69; Oxford University, later Oxford Instruments
Gottipaty N. Rao, 1967-70; IIT Kanpur, now Adelphi University
Paul Bagus, 1968; University of North Texas
Steven Koicki, 1969-70; Boris Kidric Institute, Serbian Academy of Science, Belgrade
T. Darrah Thomas, 1970, 1972; Oregon State University
Lothar Ley, 1972-73; MPI f. Metallforschung, now Erlangen University
Kenneth S. Krane, 1972-74; Oregon State University
Joachim Stöhr, 1975-77; Stanford University and LCLS

… and many others after 1976, or for short visits, some of whom will be mentioned in other talks…

Farewell to Hyperfine Interactions

At the third conference in the 'Hyperfine Interactions' series, HFI-III held in June, 1974 in Uppsala, David Shirley gave what was probably his last talk on the subject of hyperfine interactions. It was reprinted in *Physica Scripta* the following year:

Physica Scripta. Vol. 11, 117–120, 1975

Hyperfine Interactions and ESCA Data[1]

D. A. Shirley

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, Calif., USA

Received June 10, 1974

Although the group continued to publish in the field for several years, no new projects were started and the emphasis shifted entirely to photoelectron spectroscopy. Nevertheless, HFI activities were strong in the years 1970-76 due to several postdocs, including ***G.N. Rao, Günter Kaindl, Heinz Haas, Heinz-Eberhard Mahnke, Herbert Rinneberg*** and ***Ken Krane***. They were joined by several graduate students: ***Frederick Bacon, Sammy Hung, Tom Koster, Dan Salomon, Arthur Soinski*** and ***Roger Pollak***.

Mid 1970‘s

David Shirley and Eckart Matthias around the time of HFI-III in Uppsala, June 1974. Taken somewhere in Sweden.

David Shirley and Eckart Matthias with their sons, and Charles Johnson (*right foreground*), planning a camping trip. (Berkeley, 1975)

Conclusions

I would like to close on a personal note. It is almost 50 years since I started graduate work in the Shirley group at UC Berkeley; looking back from that perspective, I have very positive memories of the group, best expressed by a quote from the auto-biography of John Wheeler:

"What does a young researcher need at the beginning of a career? Perhaps, most of all, a good mentor... And freedom – freedom to experiment with ideas, freedom to try new directions, freedom to make mistakes, freedom to think without distraction.. " (J.A. Wheeler, 1998)

This describes the prevailing mode in Dave Shirley's group. He pointed us in the right direction, but wasn't constantly looking over our shoulders or prodding us.

Interestingly, when I worked with the group more than 10 years later during sabbaticals in Berkeley and Stanford, even though the scientific paradigm had changed completely – the students were now working in groups with large apparatus at even larger user facilities – the prevailing mood was still one of freedom, and the atmosphere in the group was positive and cooperative. For myself, and I am sure for many other former students, postdocs and visiting scientists, I would like to say a hearty,

"Thank you, Dave!".