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The EXAFS family tree: a personal history of the development of extended X-ray absorption fine structure

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This paper reviews the history of X-ray absorption spectroscopy (XAS) beginning with the first observation of an absorption edge, through the development of the modern theory and data inversion by the Fourier transform. I stop with my first trip to a synchrotron X-ray source. The study of XAS began at an exciting time for science. Wave mechanics, X-ray diffraction, X-ray scattering from non-crystalline materials experiments developed in parallel with XAS. However, the difficulty of obtaining data from conventional X-ray tubes limited the field to a potentially interesting minor subject. Only with the advent of synchrotron radiation and arrival of modern theory in the 1970s did XAS become widely applicable to fields ranging from environmental to biological sciences. Early developments in experimental technique and theory are emphasized. Since I worked in both the before-synchrotron and after-synchrotron time frames, I had the opportunity to meet some of the early scientists. A number of historical vignettes and photographs of the scientists involved in the development of EXAFS are presented.

Keywords: history; extended X-ray absorption fine structure (EXAFS); XANES; XAFS.

1. Introduction

This is a personal reminiscence of the development of EXAFS based on memory and extensive notes from the early days of EXAFS. Part of this story has previously been told (Lytle *et al.*, 1982). For a definitive complete 'History of X-ray Absorption Fine Structure', I recommend Stumm von Bordwehr (1989). It is an outstanding example of historical research and reads like a good detective story, holding your interest to the last page. In the present paper I tell my own story along with historical vignettes and photographs of some of the people and their research that were inspirational or important to me. Early developments in experimental technique and theory will be emphasized; however, I will discuss only those that were available and interesting to me at the time. Since I worked in both the before-synchrotron and after-synchrotron time frames, I had the opportunity to meet some of the early scientists. My EXAFS family tree is listed in Table 1 beginning with Röntgen who started it all. This is a personal list of events, people and their work that were important to me during the early years of my career. The study of X-ray absorption spectroscopy (XAS) began at an exciting time in science. Wave mechanics, X-ray diffraction, X-ray scattering from non-crystalline materials, electron diffraction *etc.* were all being developed simultaneously. Many of the XAS concepts and experiments developed in parallel with these other subjects; however, the difficulty of obtaining good data from conventional X-ray tubes limited the field to a potentially interesting minor subject.

2. Maurice and Louis de Broglie

Although Röntgen represents the beginning of X-ray science, the remarkable de Broglie royal family has been significant in both the world of science and the history of France. It has been said that if Maurice did nothing more than convince his younger brother, Louis, to drop his study of history and begin a career in science, he should be memorialized for that alone. But he did considerably more than that. His work in X-ray and atomic physics was innovative and important. Maurice had begun a career as a naval officer, but became interested in the exciting new world of X-rays and physics and resigned his commission. Beginning in the laboratory of Paul Langevin working on the ionization of gases by X-rays, he later built his own laboratory in his personal mansion on rue Châteaubriand. There he became the first in France to work with X-ray diffraction. During these experiments he invented X-ray spectroscopy. The experimental innovation came about when he mounted a single crystal on the cylinder of a recording barometer where the clockwork mechanism rotated it around its vertical axis at $2^\circ\ \mathrm{h}^{-1}$. As the crystal rotated, all angles between the incident beam and the diffraction planes (hence, all X-ray energies) were recorded on a photographic plate. In this way he obtained an X-ray line spectrum from the tube with sharp and diffuse lines, bands *etc.* Two of the absorption bands proved to be the K edges of Ag and Br in the photographic emulsion. *This was the first observation of an absorption edge* (de Broglie, 1913). It took a few more experiments to reach the correct interpretation of the absorption edges. After the end of the First World War, Maurice gathered a large group of young scientists, all working on X-ray diffraction or X-ray spectroscopy, at the laboratory in his home. Joining him in his work were, among others, Alexandre Dauvillier, Jean Thibaud, Jean-Jacques Trillat, Louis Leprince-Ringuet (all were major contributors to the field of X-ray science) and his young brother, Louis. Maurice's scientific work and his social position soon made him a major player in the science world.

Maurice was 17 years older than Louis. I would like to explore his role as elder brother to Louis. This vignette of brothers de Broglie in science deserves to be told. Louis had intended to study history like his grandfather, Jacques. After taking time off from studies as a radio operator in the navy during WWI, he became interested in physics. His interest began through discussions with Maurice and he began working with him. His work with Maurice and his first publications show his emergence as a scientist. His first two publications were about X-ray absorption spectroscopy (de Broglie, 1920*a*,*b*). The brothers even published a paper on X-ray spectroscopy together (de Broglie & de Broglie, 1921). In 1923 Louis formulated his initial ideas concerning the wave properties of electrons and published a brief paper. In 1924 he submitted his doctoral thesis to the Sorbonne. Legend has it that the faculty at the Sorbonne was unable to understand Louis' dissertation, so one of the faculty sent it to Einstein with a request for comments. Einstein reputedly replied that the young man in question did not so much deserve a doctorate as he did a Nobel Prize (Silver, 1998). Louis was so far out in front that no one knew what to make of his idea. However, his work had been noted. Felix Bloch (then a student at the ETH in Zurich) reminisced (Bloch, 1985): ". . . at the end of a colloquium I heard Debye saying something like, 'Schrödinger, you are not working right now on very important problems anyway. Why don't you tell us about that thesis of de Broglie, which seems to have attracted some attention.' In one of the next colloquia, Schrödinger gave a beautifully clear account of how de Broglie associated a wave with a particle and how he could obtain the quantization rules of Bohr and Sommerfeld by demanding that an integer number of waves should be fitted around a stationary orbit. When he had finished, Debye casually remarked that he thought this way of talking was rather childish. As a student of Sommerfeld he had learned that, to deal properly with waves, one had to have a wave equation. It sounded like a trivial remark and did not seem to make a great impression, but Schrödinger evidently thought a bit more about the idea afterwards. Just a few weeks later he gave another talk in the colloquium which he started by saying, 'My colleague Debye suggested that one should have a wave equation; well, I have found one.' "

Louis de Broglie's idea coupled with Schrödinger's wave equation spread like wildfire in the world of science. Everyone wanted to get into the act. Louis was invited to speak at the 5th Solvay conference in 1927 (Fig. 1). He was struggling with wave–particle dualism and had a half-formulated 'pilot wave' theory. The conference participants tore him apart. Most scientists were in favor of the probabilistic interpretation of the wave equation of Schrödinger. A few of the older scientists, Einstein and Lorentz among them, raised other objections. Also at the conference, the successful electron diffraction experiments of Davisson and Germer were announced. The discussion raged red hot and everyone that mattered had a loud opinion! This experience made a very great impression on Louis. The heated discussion and criticism of his ideas were taken personally. He could not forget it for the rest of his life and kept coming back to the problem of wave–particle dualism (de Broglie, 1960), trying to reconcile his initial insight with the demands of the quantum world and to state his ideas in a form acceptable to the world of physics. He

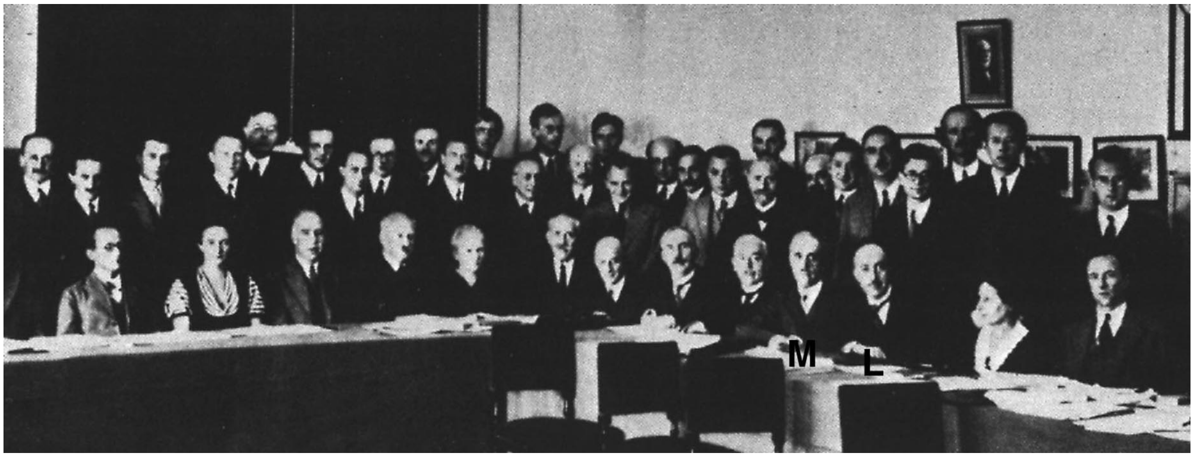

Figure 1
7th Solvay Conference; Maurice and Louis de Broglie identified by M and L.

never developed the insight and mathematical skills to fully analyze his ideas. His breakthrough had been so innovative, potentially so important and so attractive to so many others that, in a moment, his work had been wrestled away from him. He became almost a bystander, looking on. However, the timely demonstration of the reality of his ideas by Davisson and Germer resulted in great personal acclaim and he received the Nobel Prize in Physics in 1929. There is a lesson here: if you ever do something really good, the idea will spread and develop so rapidly that you will be left behind. Relax and pack your Stockholm suitcase!

3. First measurements of EXAFS

The first observations of a complicated structure in absorption edges were observed by Fricke (1920) working with the *K*-edges of compounds of Mg, Fe and Cr and by Hertz (1920) for the *L*-edges of Cs to Nd. Lindh (1921*a*,*b*, 1922, 1925, 1930) continued this work in a survey of absorption-edge structure and chemistry. Further refinement of experimental technique by Kievet & Lindsay (1930), Lindsay (1931) and by Coster & Veldkamp (1931, 1932) produced good fine-structure data for the time, which showed that metals with the same crystal structure had similar fine structure. However, both groups made a fundamental mistake in interpretation by attempting to explain their data as simultaneous transitions of two or more electrons as a result of absorption of a single X-ray quantum (Wentzel, 1921). With considerable insight into the essence of the problem, Hanawalt (1931*a*) investigated the effect of increasing the temperature of an Fe absorber. He also performed a series of long-range-order *versus* short-range-order experiments (Hanawalt, 1931*b*) on gaseous absorbers (Hg, Zn, Kr, Xe, Se and AsH_3), which only showed near-edge structure, and on solid/vapor pairs (As, $AsCl_3$, As_2O_3, $NaBrO_3$ solid and solution), which showed similar fine structure for both states of matter. “While it is true that the structure shown by vapors differs in details from that displayed by the same substance in the solid state, yet the outstanding observation is the high degree of familiarity between them. This fact probably means that the same explanation should be applicable to both of them.” When I began research in EXAFS, this early work of Hanawalt† and the later similar work of Sawada *et al.* (1955, 1959) convinced me that EXAFS was a short-range-order phenomenon.

Table 1
My EXAFS Family Tree.

Röntgen (1895)	Discovered X-rays
Maurice de Broglie (1913)	Measured first absorption edge
World War I (1914–1918)	
Fricke (1920)	Observed first fine structure
Kossel (1920)	First theory of XANES
Hanawalt (1931)	EXAFS in gases, temperature effect
Kronig (1931)	First theory of EXAFS
Cauchois (1932)	Curved crystal transmission spectrograph
Hayasi (1936, 1949)	Theory of EXAFS
World War II (1941–1945)	
Sawada (1955)	Amorphous/crystalline polymorphs
Shiraiwa (1958)	Improved theory
Kostarev (1939, 1946)	Theory and measured EXAFS in single crystals
Kozlenkov (1960)	Improved theory
Van Nordstrand (1960)	Instrumentation, fingerprint ID, used XAS to characterize catalysts
Lytle (14 July 1960)	Starts work at Boeing (BSRL)
Krogstad (1960)	Personal communication
Lytle (1962)	Particle-in-a-box model
Prins (1964)	Helped name EXAFS
Parratt (1965)	Personal communication; *Rev. Mod. Phys.* (1959). **31**, 616
Sayers, Stern, Lytle (1968–1971)	Modern theory, Fourier transform of EXAFS
Sayers, Stern, Lytle (1974)	First trip to synchrotron (SSRL)

Attempts to explain the early EXAFS measurements were advanced by Kossel (1920) and by Wentzel (1921). Kossel’s theory involved transitions of electrons to higher unfilled orbitals of the absorbing atom, very similar to the XANES theory of today. However, by no stretch of Kossel’s theory could one explain fine structure that

Figure 2
Yvette Cauchois.

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† I met Hanawalt in the 1980s while giving a seminar at the University of Michigan. He was then Professor Emeritus and came to the seminar armed with copies of all his early XAS papers. He took me to task for not mentioning his work during my seminar and presented me with his reprints. I was able to assure him that I had cited his work in my early papers and later sent him copies. Hanawalt is best known for his work in powder X-ray diffraction and the Hanawalt–Rinn–Frevel system for indexing powder patterns developed while working for Dow Chemical Co. (1931–1963). After retirement from Dow he became a professor at the University of Michigan until retirement in 1972. He died on 26 June 1987. Obituary (1987) in *Powder Diffr. J.* **2**, 266.

extended beyond a few hundred eV. Wentzel's theory assumed that this high-energy structure was caused by multiple electron excitation. The sums and differences of the binding energies of atomic electrons combined with the poor quality of the early measured spectra allowed for the 'satisfactory' interpretation of data for a number of years.

Early in a long career devoted to the study of the emission and absorption of X-rays, Yvette Cauchois (Cauchois, 1932, 1933), Fig. 2, developed the transmission bent-crystal X-ray spectrometer. This instrument allowed rapid accurate measurement of absorption edges. For 40 years it was used for short-wavelength spectroscopy in many laboratories of the world. The modern equivalent is the dispersive spectrometer with a linear array detector (Tolentino *et al.*, 1989). Cauchois & Mott (1949) published a notable paper summarizing and interpreting the science to that date. In 1964 I met Yvette Cauchois at her Laboratoire de Chimie-Physique, Université Pierre et Marie Curie. Her laboratory made an indelible impression. This ancient laboratory was filled with equally ancient X-ray generators. All were powered by mechanical spark interrupters, each rattling away to produce the alternating high voltage necessary for the X-ray tubes. Occasionally she would flip one with her finger to restart it.

4. First theories of EXAFS

Ralph Kronig, Fig. 3, published the first theory of X-ray absorption fine structure which contained some of the basic concepts of the modern interpretation (Kronig, 1931, 1932). Stumm von Bordwehr (1989) gives a detailed description of the life and accomplishments of Kronig, even recounting how his name was changed to Ralph de Laer Kronig.† Kronig & Penney (1931) published a one-dimensional model of a crystal that showed how the electrons in a crystal would be dispersed into allowed and forbidden bands by scattering from the extended linear array of atoms. His first theory (Kronig, 1931) of EXAFS was the three-dimensional equivalent of this model,

$$W_n = n^2(\alpha^2 + \beta^2 + \gamma^2)/(8ma^2). \qquad (1)$$

The theory showed that a photoelectron traversing a crystal lattice would experience permitted and forbidden zones depending on its wavelength and that, even when the effect was averaged over all directions in the lattice, a residual structure should be observed. It was successful in predicting many generally observed features of the fine structure, including similar structure from similar lattices, inverse r^2 dependence, correct r *versus* T dependence and increasing energy separation of the fine-structure features with energy from the edge. The equation, which was re-derived in a more quantitative way in 1932,

$$W_n = h^2(\alpha^2 + \beta^2 + \gamma^2)/(8ma^2 \cos^2\theta), \qquad (2)$$

was simple to apply and interpret. Every experimenter found approximate agreement with the theory. There were always some absorption features close to that predicted by the possible lattice planes. However, the expected strong reflections [*e.g.* (100), (110), (111) *etc.*] did not always correlate with the most intense absorption features as intuitively expected. Still, agreement was close enough to be tantalizing and *everyone* tested the agreement of their measured 'Kronig structure' with the simple Kronig theory. In equation (2), energy positions W_n correspond to the zone boundaries, *i.e.* not the absorption maxima or minima, but the first rise in each fine-structure maximum. α, β and γ are the Miller indices, a is the lattice constant and θ is the angle between the electron direction and the reciprocal lattice direction. When averaged over all directions with a non-polarized X-ray beam and a polycrystalline absorber, $\cos^2\theta = 1$. However, with a single-crystal absorber and polarized X-rays the absorption features should be larger for specific crystal planes. This was another experimental variable that might verify the theory and many attempted to test it. Thus began the long record of publications in which Kronig structure was interpreted in terms of the simple Kronig theory. Until the 1970s, fully 2% of the

Figure 3
Ralph Kronig.

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† I met Kronig in Delft in 1964 at The International Conference on Physics of Non-Crystalline Solids. After my presentation he asked a probing question and we continued the discussion afterward (see Lytle, 1965). Still alive in 1986, he was invited to the Fontevraud Conference, but poor health prevented his attendance. Kronig died on 16 November 1995. Obituary (1997) in *Physics Today*, March 1997, pp. 97–98. "In physics Kronig ranged far and wide. He derived the Kramers–Kronig dispersion relations connecting the indices of refraction and absorption as early as 1924. He also wrote several papers in other fields; most influential were the Kronig–Penny model for solid-state physics and the Coster–Kronig transition in atomic physics." Nowhere in the quoted obituary (or the one published in Dutch, Delta nr. 37, donderdag 30 November 1995, jaargang 27, 3 pages) is there any mention of his contributions to the theory of X-ray absorption fine structure.

papers published in *Physical Review* were devoted to X-ray absorption spectroscopy and most invoked Kronig's theory. The short-range-order data of Hanawalt (1931*b*) stimulated Kronig (1932) to develop a theory for molecules,

$$\chi = 1 + (1/2) \int_0^{\pi} \sin\theta \, \mathrm{d}\theta \, [(q + q^*) \cos\theta + |q|^2]. \quad (3)$$

This model served as the starting point for all the subsequent short-range-order theories but few attempted to compare it with their data. Kronig's student, H. Petersen, continued this work (Petersen, 1932, 1933). His equation,

$$\chi(E) - 1 = \sum_{l=0}^{\infty} (2l + 1)[(-1)^{l+1}/(k\rho)^2][\sin(\delta_l) \sin(2k\rho + \delta_l)], \quad (4)$$

shows many of the features of the modern theory. This theory was applied to $GeCl_4$ by Hartree *et al.* (1934). A description of the Herculean efforts required to perform the calculations can be found in Stumm von Bordwehr (1989).

In Japan, Hayasi† (1949), Fig. 4, attempted to apply Kronig's equation, (2), to explain his data and noted that the equation predicted much more structure than was observed. He reasoned that when the electron encountered the periodic potential of the strongest planes it would be reflected back toward the absorbing atom. He called this a 'quasi-stationary state' and concluded that the dipole matrix element would be larger, hence greater absorption, than for electrons which freely propagate in the crystal. His equation,

$$V \simeq 150N^2(l^2 + m^2 + n^2)/4w^2, \quad (5)$$

bears a remarkable similarity to that of Kronig and was equally successful in explaining experimental spectra. Also in Japan, a group led by M. Sawada *et al.* (1959) began with Kronig's equation (2) and tested much experimental data. They finally concluded that the fine structure was determined by the immediate surroundings of the absorbing atom. Their theory (Shiraiwa *et al.*, 1958) calculated the fine structure from individual atomic scattering and included a lifetime term to limit the effect to short range,

$$\begin{aligned}\chi(k) = {} & \sum_s (2\pi/k^2 r_s^2) \exp(-1\mu r_s) \\ & \times \Big[-\sin 2kr_s \sum_l (-1)^l (2l + 1) \sin 2\eta_l \\ & + \cos 2kr_s \sum_l (-1)^l (2l + 1)(\cos 2\eta_l - 1) \Big]. \quad (6)\end{aligned}$$

All this (and other Japanese) work is summarized by Stumm von Bordwehr (1989).

In Russia, work on EXAFS had begun in the 1930s, but the research was little noted in the west. When some Russian journals became available in English translation their work became more widely known. Kostarev's (1941) second paper [and subsequent work through 1971; see Stumm von Bordwehr (1989)] was particularly instructive in that the theory was cast in terms of nested coordination shells, *i.e.* a short-range-order theory, and included a scattering atom phase shift,

$$\begin{aligned}\chi(k) = \Big\{ & 1 + 2/k \sum_{i=0}^{\infty} \big[(I_i')^2 + (I_i'')^2\big]^{1/2} \\ & \times \sin\big[2(k\eta_i + \delta) + \arctan(I_i'/I_i'')\big] \Big\}^{-1}. \quad (7)\end{aligned}$$

Building on the work of Kronig, Shiraiwa and Kostarev, A. Kozlenkov‡ (1961), Fig. 5, developed a short-range-order theory which is shown in general form as

$$\tau(k) \simeq \big[1 - A(k) \textstyle\sum (N_s/r_s^2) \sin(2kr_s + 2\eta_1)\big]^{-1}. \quad (8)$$

He showed that the phase shifts of the different atomic species could be separately calculated or derived from experimental spectra. This theory was very close to the modern theory.

In the United States, Robert Van Nordstrand§ (1960, 1967), Fig. 6, made modifications to a commercially available Norelco diffractometer so that absorption spectra could be obtained using conventional diffraction X-ray tubes as the source of X-rays. He used automatic step scaling to scan through the absorption edge. In the position of the diffraction sample he placed a crystal of Si or quartz as a single-crystal monochromator. Although the resolution was not as good as with a double-crystal monochromator, it was sufficient to obtain useful spectra. The thin absorption sample was mounted in the beam path. First, I_0 was measured, point by point, over the full range of the scan, then the absorber was placed into the beam and I_1 was measured. The absorption coefficient was calculated as ln I_0/I_1 and normalized to unit absorption edge jump. He completed a study of the spectra of many transition metal

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† I initiated correspondence with Hayasi and he responded with encouragement and reprints of his work. We shared German as a common written language, his was fluent and mine was marginal.

‡ In preparation for this paper I sent an e-mail to all those I knew about in Russia who might know of Kostarev (nothing ever turned up on Kostarev) or Kozlenkov. I thank Alexander Lebedev, Moscow State University, who soon replied with a scanned photograph of Alex Kozlenkov. A short time later I received the following e-mail from Kozlenkov himself, "My photograph required for your review of the EXAFS history was scanned and sent to you by one of my colleagues . . . The same request was received from Dr Y. Babanov, Ekaterinburg and Professor A. Vinogradov, Levedev Physical Institute, Moscow. I hope that you have already received the photo . . ." One can imagine his consternation. Suddenly everyone wanted his picture. What's going on? Since that time Kozlenkov and I have enjoyed a continuing e-mail correspondence. He is still interested in the theory of EXAFS and plans a review of the early Russian work. He works in the Nauka Publishing (Russian Academy of Sciences) as a translator and editor of a number of Russian scientific journals.

§ Bob Van Nordstrand is hale and hearty at 82 enjoying retirement in San Rafael, CA. He described his professional life, "My career started in 1942 at Sinclair Research in Harvey, IL. Local management became jealous of my progress and publications, so they sent me to Tulsa in 1962 to work on exploration and production of oil. Then Arco bought Sinclair and they shut down the Tulsa Laboratory. I taught chemistry and physics at the University of Tulsa for a couple of years, then went to Los Angeles to work for Filtrol, the catalyst manufacturer. They fired me in 1977 after five years. Chevron hired me to work on zeolites. After 15 years with Chevron I retired in 1992. I had a good life. The best were the years at Sinclair when I worked on adsorption, X-ray diffraction, small-angle X-ray scattering and X-ray spectroscopy, all applied to developing catalysts."

compounds and classified their spectra according to the atomic structure and valence of the element in the compound, also noting the chemical shift with valence. This fingerprint classification was used to identify the structural/valence form of elements in catalysts, which are usually so highly dispersed that their diffraction patterns cannot be measured. This work of Van Nordstrand was the first example of the application of XANES/EXAFS to the routine investigation of structure. He concluded, “For study of the chemistry of catalysts and other non-crystalline systems this technique may have a role comparable to that of X-ray and electron diffraction in crystalline systems.” Van Nordstrand’s work was formative in beginning my experimental program at Boeing and in the application of EXAFS to the study of non-crystalline materials.

5. I begin research at Boeing

Before arriving at Boeing my education and previous employment background were in the use of X-ray diffraction and fluorescent X-rays for chemical analysis. Discharged after two years of active duty in the US Army Artillery, I was hired at the Boeing Scientific Research Laboratories (BSRL) in 1960 as their X-ray expert. BSRL was Boeing’s basic research organization and I was invited to submit a research proposal and given the assurance of continuing adequate funding to carry it out. Through reading the old and current literature I had become familiar with the status of X-ray absorption spectroscopy and become fascinated with the potential for structural information. But I had never performed an experiment. The confidence of youth is amazing! So in 1960 I submitted the following proposal:

> **A Study of Electronic Structure by X-ray Spectroscopy**
>
> **I. Introduction**
>
> X-ray spectroscopy can provide accurate information about the electronic structure of materials. Any type of substance . . . crystal, liquid or gas may be studied . . . X-ray absorption provides a view of the states corresponding to the unoccupied outer electronic levels. Both emission and absorption data lead directly to bond energy and type.
>
> **II. Fine structure of X-ray absorption spectra**
>
> In the X-ray absorption process an incident X-ray photon removes an electron from its shell to either an outer unoccupied level or someplace outside the atom. Neighboring atoms have an effect on the outermost levels and distort and impose a complex level structure. Consequently, one observes a ‘fine’ structure about the main absorption edge dependent upon the state of the absorber . . . Finally, there is an extended fine structure (Kronig structure) which has been interpreted as being due to the interaction of the ejected electron with the crystal lattice. *It is planned to study various pure elements, compounds and alloys in an attempt to correlate X-ray absorption structure with type of bonding and solid state structure* . . . According to the Kronig theory, polarized X-rays incident upon a thin single crystal should yield a structure which varies with crystal orientation . . . An attempt will be made to prepare thin single crystals to test this . . . X-ray analyzing crystals . . . available should allow a choice for adequate polarization.

In retrospect it appears that I did a good job and stand amazed at the small decisions which direct one’s career!

After reporting for work I found that a member of the group, R. S. ‘Max’ Krogstad, had been a student of S. Town Stephenson. His thesis research had been a study of X-ray absorption spectroscopy, in particular attempting to verify

Figure 4
Takesi Hayasi.

Figure 5
Alex Kozlenkov.

the effect of polarization on the Kronig structure (Krogstad *et al.*, 1953). Although Max was working on different topics and we never collaborated on research, he proved to be a wonderful resource on the subject of X-ray spectroscopy and an enthusiastic foil for testing my ideas. Following the lead of Van Nordstrand (1960), I converted a Siemens horizontal diffractometer to a single-crystal X-ray spectrometer (Lytle, 1966; Lytle *et al.*, 1975). The horizontal arrangement made it possible to easily insert a cryostat into the beam path to cool the absorber. The first experiments measured the temperature effect (Lytle, 1962*a*). The spectrometer was automated with stepping motors and automatic sample movement in and out of the beam. I found that the intensity of the impurity element lines in the X-ray tube changed too rapidly for the alternate I_0/I_1 scanning scheme of Van Nordstrand (1960). Data were punched on IBM cards for computer calculation and plotting of the spectra. Low-temperature spectra were accumulated with quality sufficient for a definitive test of the simple Kronig (1931, 1932) theory including the effect of polarized X-rays and single-crystal absorbers. It soon became apparent that there was only occasional agreement between the measured absorption features and the energy positions predicted by the simple Kronig theory. Also, there was no change in the absorption features with polarization for single-crystal absorbers of Cu or Ge. The simple Kronig theory did not work! My own measurements and the data on crystalline/amorphous polymorphs of Hanawalt (1931*a*,*b*) and Sawada *et al.* (1955, 1959) convinced me that the EXAFS was a short-range-order effect determined primarily by the first neighbors.

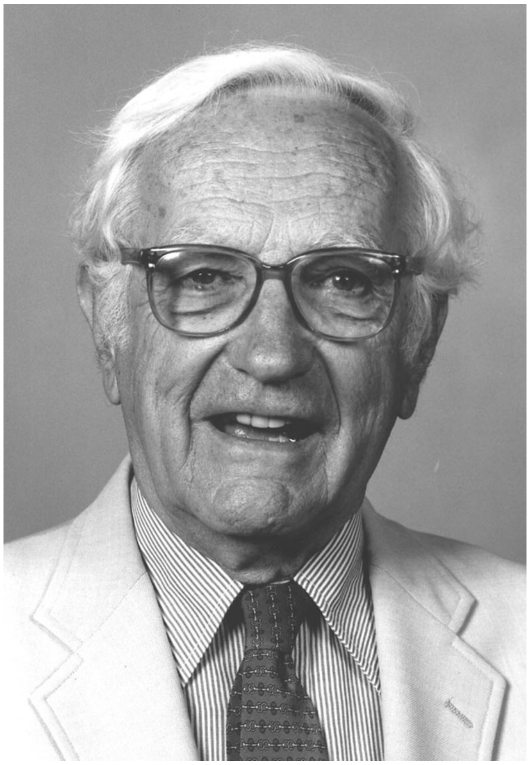

Figure 6
Bob Van Nordstrand.

5.1. *An ad hoc theory: a break from Kronig structure to EXAFS*

I decided to begin anew with the experimental data. I was very familiar with indexing X-ray diffraction powder patterns and wanted to ‘index’ the EXAFS pattern. Some variable had to be related to structure in a simple way. Starting with experimental data from amorphous solids (*e.g.* Ge, GeO_2 and Se) for which the EXAFS was almost a single sine wave, I constructed a one-dimensional plot marking the positions of the primary absorption maxima along an energy scale in eV. The plots for different materials were similar and, by making accordion-like adjustments, all the plots could be overlaid approximately. What was the meaning of the increasing energy interval between the absorption maxima in each spectrum as the energy increased? Was there some natural function that would account for it? Through a purely trial-and-error approach I soon discovered that the energy scale of the absorption spectra was proportional ($E \propto Q$) to the zeros of the half-order Bessel function, Q (Jahnke & Emde, 1945), which appear in the solution of the wave equation for a particle in a spherical cavity (Kauzmann, 1957). This correlation was presented (Lytle, 1962*b*).

Inspired particularly by Kostarev (1941) and Kozlenkov (1961), who cast their theories in terms of nested coordination spheres, a model of EXAFS was constructed in which the absorbing atom was surrounded by the first-neighbor Wigner–Zeitz atomic polyhedron which was characteristic of the lattice. The polyhedron was further approximated by a sphere of equivalent volume. Then the solution of the wave equation in a spherical cavity with zero potential inside and infinite potential at the boundary, *i.e.* forcing the wave function to go to zero at the boundary, is equivalent to the textbook case (Kauzmann, 1957) of an electron in a spherical box,

$$E = h^2 Q/8mr_s^2. \qquad (9)$$

The absorption maxima occur when Q is a zero root of the half-order Bessel function appearing in the wave equation. In units of $h^2/8mr_s^2$, $Q = 2.04, 6.04, 12.0, 20.0, 30.0, 42.0$ *etc.* To obtain the first-neighbor distance, r_s, one can plot E *versus* Q and evaluate r_s^2 from the slope,

$$E = (37.6/r_s^2)Q. \qquad (10)$$

This simple method of data analysis worked well and r_s could be determined to an accuracy of a few percent (Lytle, 1965, 1966). Because of this almost trivial technique for extracting information from EXAFS, the method had a life of its own into the 1970–1980s in areas of the world where electronic computers were not available (*e.g.* Agarwal & Johri, 1977). This theory of EXAFS threw away everything known about electron scattering from atoms. Although the model included only the first-neighbor distance and spherical symmetry, it worked well enough to extract that bond distance from the data. Why? Because it contained a number of grains of truth. The symmetry was assumed to be spherical, averaging over the nearest neighbors. As is now well known, the EXAFS is heavily weighted by the first neighbors, particularly in close-packed structures and at room temperature, so the eye easily picks out the main bump from the secondary structure. When working in energy units rather than k units, Bessel functions are the natural variable. The zeros of the Bessel function in eV correspond to the zeros of $\sin(2kr)$ in k units (Å^{-1}). The plot of E *versus* Q is equivalent to plotting k *versus* n, where n corresponds to the zeros 1, 2, 3, 4, 5, 6 . . . of the sine function for the first, second, third . . . absorption maxima. For comparison, this equivalent analysis in k units was demonstrated by Lytle *et al.* (1975).

This simple theory and selected experimental results were presented in 1964 at the International Conference on Physics of Non-Crystalline Solids (Lytle, 1965) hosted by Professor J. A. Prins, Fig. 7. Prins was best known for his early work on X-ray scattering from non-crystalline materials (Zernicke & Prins, 1927) for which they used the Fourier integral theorem to invert X-ray scattering data. At the conference, although personally unknown to me, was Professor Kronig. After my presentation both Professor Prins and Professor Kronig asked questions [published in Lytle (1965)] concerning the apparent success of my simple model even without an accurate field to describe the electron scattering. Their comments indicated to me that both of them knew a lot about the problem. We had a good conversation afterwards and both encouraged me to continue my research. When the manuscript was submitted to Professor Prins for publication in the proceedings, I wanted to make a clean break with 'Kronig structure' and referred to the fine structure by the acronym XAFS (X-ray absorption fine structure). In a series of letters, Professor Prins, who was very much a formidable 'Herr Professor', informed me that he did not like acronyms and XAFS was not accurate anyway because it implied that the 'Kossel structure' could be included also. Personally, I think that he did not like the idea of expunging the name of his friend and colleague from this physical phenomenon. He finally agreed on EXAFS as being both 'accurate and euphonious'. Thus, *Professor J. A. Prins passed editorial approval of the name EXAFS.* There is more to say about Prins' possible involvement in EXAFS later.

Professor Lyman Parratt, Fig. 8, of Cornell University was active in the field of X-ray absorption spectroscopy, particularly for near-edge structure. He and his students published a number of significant papers, such as Parratt & Jossem (1955). Parratt hosted a conference on the Physics of X-ray Spectra, Ithaca, NY, in June 1965. I sent him a preprint of my research on determining bond distances using the particle-in-a-box theory of EXAFS and he invited me to give a paper at the conference. From this meeting and the following discussions we found that we shared a common heritage, born in Utah from Mormon pioneer stock. While at the conference he invited me to his home for lunch and introduced his family. In the years following he was supportive of my research efforts, occasionally

Figure 7
Jon Prins.

Figure 8
Lyman Parratt and Leonard Jossem.

directing me to significant publications. 40 years later his paper ‘Electronic Band Structure of Solids by X-ray Spectroscopy’ (Parratt, 1959) can still be read productively to gain information into the physics of X-ray processes and to marvel at his insight. [Lyman Parratt died on 29 June 1995. Obituary in *Physics Today*, August 1996, p. 81.]

6. Collaboration with Edward A. Stern and Dale E. Sayers, Fig. 9

I first met Ed Stern in 1966 when he was hired as a summer employee at BSRL. Soon thereafter he became a consultant (October 1967–October 1968 for 12 days for the grand price of $200 per day) to the Solid State Physics Group in which I was working. In due course I talked with him about my X-ray absorption spectroscopy research. It was apparent to him that a more detailed and accurate inclusion of the physics of the effect would much improve the theory. My model did not contain much of the solid-state-physics theory that he knew so much about. In May 1968 he called to inquire about a summer position for a starving student, Dale Sayers. I had a busy laboratory collecting EXAFS data on many materials. Dale joined in the experimental work and, with help from Ed and I, began thinking about the physics of EXAFS as a Master’s thesis problem. By July 1969 this collaboration had blossomed into a new ‘Point Scattering Theory of EXAFS’, which was published as a Boeing document (Sayers, Lytle & Stern, 1969) and presented at the 18th Denver X-ray Conference (Sayers *et al.*, 1970). The abstract states, ‘We calculate the EXAFS by treating the ejected photoelectron as a spherical wave which expands in the lattice and is partially scattered by neighbors of the absorbing atom. The neighboring atoms are treated as point scatterers and the total scattered wave is summed from the waves scattered by each atom. The fine structure is determined from the dipole transition matrix between the initial K-state and the final photoelectron state. Calculations compare favorably with experimental data.’

Figure 9
Ed Stern, Dale Sayers and Farrel Lytle.

The final equation,

$$\chi = V_0 k \ \times \sum_j \frac{\exp(-\gamma r_j)}{k' r_j^3} \left[\left(\frac{2\,\mathrm{sum}\,Z_j}{r_j^2} - N_j \right) \alpha_j - \frac{(k\,\mathrm{sum}\,Z_j \beta_j)}{r_j} \right], \quad (11)$$

is formidable. However, we had entered the modern era of electronic computers to evaluate the equation and compare with a variety of data. The theory was very successful in calculating the EXAFS from materials with known structure. Since Dale had now completed his MS degree, the normal Boeing wage scale would have been a decent salary. But the University of Washington powers-that-be decided that a living wage would be unfair to other students and insisted that he be paid, part-time, at the rate of a graduate student fellowship. So we kept him starving.

6.1. *‘May you live in interesting times’ – old Chinese curse/blessing*

Ed was due a sabbatical for the 1970–1971 school year. He felt it safe to leave Dale with me for a year, so I was named to Dale’s thesis committee. The world economy was slowing down and rumor had it that things would become tight at Boeing. In a group meeting our BSRL supervisor, Hans Brunner, suggested that everyone who could write a proposal to obtain outside funding for their research should do. Ever the dutiful employees, Dale and I prepared and submitted a proposal (1969) for ‘Investigation of the Structure of Non-Crystalline Materials by Analysis of the Extended X-ray Absorption Fine Structure’ to the Army Research Office. Ed was to be a consultant. This promised to be a combined experimental and theoretical effort directed at a variety of amorphous materials. The theoretical effort was to be (i) generalization of format to include more complex lattices and defect structures, (ii) extension of theory to lower energies, (iii) more accurate methods of phase calculation and (iv) development of a program for multiple curve fitting to be used for quantitative data analysis. It is amusing now but it was state-of-the-art then. We bragged that our computing power was an IBM 360-44 system *with 256000 byte core memory – WOW!*

Then the layoffs at Boeing began. One of the first to go was Dale as a part-time employee. However, Ed’s research grant was sufficient to pick him up and our joint research continued. A plan for Dale’s PhD thesis research was adopted with experimental work to be performed with me at BSRL supported by frequent correspondence with Ed in Israel (no e-mail then). The success of the Point Scattering Theory in calculating EXAFS in a variety of materials had confirmed our ideas about the short-range nature of EXAFS and the structural information contained therein. How could one go the other way and determine structure from EXAFS? Shortly before Ed left on sabbatical the three of us met in Ed’s office for an attempt to invert Sayers *et al.*'s equation, (11). The complexity of the equation defied these initial attempts; however, the seed had been planted. This became an almost unspoken but primary goal of the research. Successful inversion of EXAFS data would present structural information in a unique new way.

6.2. *Success!*

In a letter to Ed in the fall of 1970, Dale pointed out a simplification of equation (11). Finally, early in 1971 he realised how to apply the Fourier integral theorem and invert it. *In a defining moment, I can still visualize Dale's excitement as he ran down the hall to greet me with the first plot of the first Fourier transform of the EXAFS function of germanium!* Within a week Dale received a letter from Ed where Ed had performed the same mathematical inversion at approximately the same time. The new Fourier transform analysis of EXAFS was presented at the Cleveland Meeting of the American Physical Society, 29 March 1971 (Sayers, Lytle & Stern, 1971) and soon published (Sayers, Stern & Lytle, 1971). Perhaps it was to be expected, but the one referee for this paper who appeared to have had some experience in X-ray spectroscopy rejected it as being trivial and unimportant. ('New ideas are always suspected and usually opposed without any other reason than because they are not already common,' John Locke.) However, the other referees appreciated the significance and it was published with little revision. As part of his PhD thesis program, which was completed in June 1971 (Sayers, 1971), Dale applied the Fourier transform analysis technique to EXAFS data from a variety of crystalline and amorphous materials.

Later in 1971 our grant from ARO was approved but the grant coincided in time with the total dissolution of BSRL and much of the rest of The Boeing Company. During the 1970–1971 period Boeing laid off two-thirds of its employees and liquidated many facilities in a successful attempt to avoid bankruptcy. The entire BSRL support staff, our scientific colleagues and management, all either managed a transfer or received their lay-off notices. Dale was already gone, but I was not laid off. Somewhere in what little remained of Boeing it had been noted that not only was there funding from ARO but also a profit for Boeing. The ARO research grant contained full support for Dale and me with Ed as a consultant for three years of research. The BSRL laboratory building was essentially abandoned. For example, the library book shelves were sold out from under the books which were dumped on the floor. State-of-the-art laboratory equipment was sold for 10% of its value. For the remainder, there was no security and scavengers from the street hauled things away. Personally, I was left alone in an empty building, with no electrical power, attempting to defend my laboratory equipment from scavengers while trying to find a management structure within the remaining Boeing company to report to. *Having once experienced such a trying time in my professional life, nothing ever afterwards was surprising or even remarkable.* Eventually a Boeing organization accepted us and our grant. Dale was rehired and our collaboration continued. This grant, which was funded by the Advanced Research Projects Agency (ARPA, the research arm of the Pentagon) and administered by Charles Boghosian of the Army Research Office, Durham, was absolutely critical to the continuation of our research and collaboration. After this time Boeing no longer funded any basic research. (See Grants/Contracts in the Acknowledgement.) Since our proposal emphasized amorphous semiconductors our papers addressed that topic (Sayers *et al.*, 1972, 1974) and explored applications to catalysts (Lytle *et al.*, 1974) and biological materials (Sayers *et al.*, 1975). The complete EXAFS technique to that date was published in three papers: theory (Stern, 1974), experiment (Lytle *et al.*, 1975) and determination of structural parameters (Stern *et al.*, 1975). During this period considerable effort was devoted to the problems of data analysis, *e.g.* pre-edge removal, data normalization, splines, FFT, zero filling, transform windows *etc*. The Boeing analysis package was developed by Paul Franz (Franz *et al.*, 1973). This program was the grandfather of many of the later US analysis packages. Until that time all of the data had been obtained with the conventional X-ray sources in our Boeing laboratory. Then the Stanford Radiation Research Project started and you know the rest of that story. In one trip to the synchrotron we collected more and better data in three days than in the previous ten years. I shut down all three X-ray spectrometers in the Boeing laboratory. A new era had arrived!

7. Why did it take 40 years?

As noted above in the historical introduction, most elements of the modern theory of EXAFS were appreciated in the 1930s and certainly by the 1940s. Why was it not until 1971, when EXAFS data was first Fourier transformed, that the potential for structure determination was appreciated? The history of EXAFS has a close analogy with the early work on X-ray scattering from non-crystalline materials. Debye (1915) showed that any group of atoms must cause X-ray diffraction; crystalline order was not necessary. After considerable experimental and theoretical work and a number of false starts, Zernicke & Prins (1927) provided the starting point for the interpretation of X-ray scattering data. They showed how to apply the Fourier integral theorem to determine the two-body correlation function of the X-ray scattering material. In retrospect, the near coincidence in time and the presence of at least one person who worked on both X-ray scattering and X-ray absorption fine structure suggest that EXAFS should have been understood and inverted then rather than waiting for so many years. J. A. Prins, who co-authored the paper on Fourier transformation of X-ray scattering data (and much later participated in the naming of EXAFS), also worked and published in X-ray absorption spectroscopy (Prins, 1934). He could have made the connection between X-ray and electron scattering. But it was clear that a confusion over the short-range-order *versus* long-range-order (simple Kronig theory) nature of EXAFS persisted until 1971. The experimental data were difficult to obtain, the comparison with theory was difficult to calculate and the theories were not quantitatively accurate. Look at the equations in this paper and imagine comparing data with them if you were armed with a slide rule to evaluate them. Just as everyone else, you would compare your data with Kronig's simple equation (2) and report partial agreement. As in the X-ray scattering work, the turning point was the simplification of EXAFS theory to an equation which could be Fourier transformed. Immediately one is confronted with a series of peaks in a familiar format spaced like a radial distribution function (RDF). All the calculational uncertainties of phase shifts, scattering envelopes, temperature factors and mean free paths become less fundamental to an understanding of the phenomenon. Application of the Fourier transform to EXAFS data turned the phenomenon from a persistent scientific curiosity into a quantitative structural tool!

8. In retrospect

I marvel at the events of the last 40 years. Who could have imagined what has happened to the field of X-ray spectroscopy? My personal dreams began with a modest plan and very humble beginnings. But it led to the first halting steps of success and later moments of inspiration and satisfaction. The story told here would not have happened without the career-defining collaboration (for all three of us) with Dale Sayers and Ed Stern. Since the 1970s we have not collaborated on any specific scientific research project but have remained friends and collaborators in the development of facilities and contributions to improve the science of EXAFS. The near coincidence in time of a complete theory of EXAFS and the development of synchrotron X-ray sources [see, for example, Lynch (1997), Doniach *et al.* (1997)] was the final key to the advancement of X-ray spectroscopy. I stand in awe at the comparison between a third-generation synchrotron laboratory and the clanking chattering spark interrupters driving the X-ray generators that I saw long ago in Yvette Cauchois' laboratory. To witness more than 400 delegates at XAFS X compared with less than 80 who attended the first international meeting of Modern XAFS in 1981 (Garner & Hasnain, 1981) is an endorsement of the technique coming of age. I end with Harlow Shapley's statement: *To have been a participant is in itself a glory.*

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