

Musings about the development of XAFS

Edward A. Stern

*Physics Department, University of Washington, Box 351560,
Seattle, WA 98115-1560, USA.*

E-mail: stern@phys.washington.edu

A personal recollection of the development of X-ray absorption fine structure (XAFS) into a structure-determination technique is presented. Because of confusion in the theoretical explanation of the ‘Kronig structure’, now called EXAFS, the extended XAFS, its explanation remained unresolved for about 40 years. As I was introduced to the EXAFS phenomenon by Farrel Lytle and saw his impressive data, the thought came to me that scattering of the photoelectron from surrounding atoms could be the mechanism of the effect. My graduate student, Dale Sayers, agreed to work on developing the theory under my supervision and to make EXAFS measurements under Lytle’s supervision as his PhD thesis. The theory led to the idea of a Fourier transform of the EXAFS, which showed peaks from surrounding atoms, proving the validity of the theory and suggesting the method of structure determination by using standards from known structures. Within a few years, facilities at synchrotron sources were developed to measure XAFS, opening up the technique to the general scientific community. In spite of some initial growing pains, XAFS has matured into a powerful technique for local structure and has been applied to obtain magnetic structure, in addition to distribution of atoms. Other related techniques have been spawned from XAFS, expanding the impact of the original phenomenon.

Keywords: XAFS; EXAFS; XANES; development of XAFS.

1. Introduction

Permit me to thank you for the singular honor of being chosen for the International XAFS Society (IXS) Outstanding Achievement Award of Year 2000. I greatly appreciate this recognition by my peers. It means a lot to me. I am reminded that when I was actively involved in helping the Soviet Refusenik scientists during the 1970s while the Soviet Union was very repressive of human rights, the Soviets recognized the effectiveness of my activities by condemning me in a Novesti press release that included the statement that I was much better known for my reactionary Zionist activities than my scientific accomplishments. Although I never took this propaganda statement seriously, still, since I had no reputation as a reactionary Zionist, the recognition today by my peers reconfirms that Soviet officials were then not any better in judging scientific abilities than they were in observing human rights.

Firstly, I want to recognize the person who was most instrumental in my scientific life, my wife Sylvia, who tolerated sharing me with physics. Without this tolerance I could not have devoted the time necessary to accomplish what I did. Next come my students, postdocs and colleagues who taught and inspired me and carried out most of the work that helped to develop the basis of the XAFS techniques. A list is appended in the last section, giving only XAFS-related ones. Foremost among these are my initial collaborators, Farrel Lytle and Dale Sayers, without whom I would not be associated with the development of XAFS as a structure-determination technique.

This occasion provides the opportunity to give a personal recollection of my involvement in the development of XAFS as a struc-

ture-determination technique. In this recollection I will use the following acronyms: XAFS for the full spectrum of the X-ray absorption fine structure; EXAFS for the extended portion of the X-ray absorption fine structure; and XANES for the near-edge portion of the X-ray absorption fine structure. The division between EXAFS and XANES is somewhat arbitrary, but it is typically assumed to occur about 25 eV above the Fermi energy. Other discussions of the development of modern XAFS are presented by Stern (1997) and Lytle (1999). First let me go back to how I became involved with the X-ray absorption fine structure (XAFS) phenomenon.

2. In the beginning

As strange as it sounds, it actually started in the early 1930s, when I was one year old, with the three publications of Kronig. I was not as precocious as this statement may imply, as I did not know it at the time. Kronig’s first two publications (Kronig, 1931, 1932) developed what was subsequently called the long-range-order (LRO) theory (Azaroff, 1963) to explain the recently observed extended XAFS (EXAFS) phenomenon in solids. These papers related the inflection points between maxima and minima in crystalline absorbers to energy gaps in the photoelectron final-state energy spectrum that are introduced by the long-range periodicity of the solid. To explain the EXAFS in molecules required another theory and in his third paper Kronig (1932) developed for a diatomic molecule what was subsequently called (Azaroff, 1963) the short-range order (SRO) theory. This theory had the essential basic physics of the modern theory of EXAFS, namely, that the final-state energy spectrum is that of a free electron, while its wave function is modified by the scattering from its nearest neighbor atoms. His SRO calculation and subsequent extensions did not have all of the necessary quantitative and qualitative features of the modern EXAFS, but its essential basic physics was correct.

Because of Kronig’s pioneering work, the EXAFS was initially called the Kronig structure. Today we know that if the physics is correctly performed, the SRO and LRO theories are equivalent, but such was not the case in Kronig’s LRO theory because he did not have the correct basic physics. Kronig neglected the modification of the photoelectron wave function due to the scattering from its neighboring atoms, a first-order effect, and incorrectly assumed that the gaps in the energy spectrum, a second-order effect, were of paramount importance, *i.e.* he had thrown out the baby with the bath water (Stern, 1974). Although Kronig may have known better, he never published anything to dispel the idea that fermented and confused the subsequent development of the field for some 40 years, namely, that the LRO theory applied to solids and the SRO theory to molecules. This, in spite of the fact that 10 years after Kronig’s pioneering papers, Kostarev (1941) came to the correct conclusion that the SRO theory is the correct one for both solids and molecules. Kronig’s influence was still paramount. Other factors were that reliable quantitative experiments were difficult to perform and theory was not quantitative enough to calculate the photoelectron–atom scattering interaction, so there was no convincing agreement between SRO and experiment. In a review of the status of EXAFS up to 1970 (published in 1974) (Azaroff & Pease, 1974) it is stated, “. . . it is premature to draw any conclusions regarding the most appropriate calculational approach to employ [for EXAFS]”. A clever experimental study of EXAFS that attempted to distinguish between the SRO and LRO theories (Perel & Deslattes, 1970) stated in its summary, “Neither of the [EXAFS] theories discussed [SRO and LRO] can account for even the ‘gross’ characteristics of the absorption spectra”. Kostarev learned by disappointment that it is

not enough to be correct in physics, one must also be convincing. The correct way to be convincing had not yet arrived.

3. My enlightenment

Now let us move to 1965, when I left the University of Maryland to join the University of Washington. Again, I must thank my wife for this move since Seattle, where the University of Washington is located, is her place of birth and where she prefers to live. At that time, during the golden age of physics, the Boeing Company had the Boeing Scientific Research Laboratories (BSRL), where basic research was being carried out. I became a consultant at BSRL and had the opportunity to talk to various researchers there. The meeting with Farrel Lytle was the one that had the biggest impact on me. He told me about his work on EXAFS. I had never heard about this phenomenon before and was struck by the fact that there was no understanding of the effect. I found out only later that I was indebted to Kronig for this. As I listened to Farrel, the physics of the phenomenon became self-evident. The photoelectron wave function would be scattered by surrounding atoms and the interference between the back-scattered and outgoing waves would modulate the absorption matrix element. Being ignorant of the previous history of the theoretical confusion about the Kronig structure, I was not encumbered by the legacy.

4. Thesis problem

When I returned to my office I decided that this would be a good thesis project for one of my first graduate students at the University of Washington, Dale Sayers. Dale was interested, so we started developing the theory of EXAFS based on my physical picture and then planned to apply it to try to understand the EXAFS spectrum of an amorphous metallic alloy that he would measure under Lytle's supervision. Lytle had built one of the few remaining state-of-the-art facilities to measure EXAFS. This collaboration was cemented further when Dale spent the summer of 1968 working with Farrel at his busy laboratory, measuring the EXAFS of various materials. However, a problem arose. Dale's wife was no longer willing to live frugally and insisted that Dale leave graduate school and take a job to support his family. Fortunately, a compromise ensued where Dale joined BSRL to help Farrel Lytle with his experimental measurements, while being able to pursue his thesis research under my supervision. The main parts of the theory were formulated by the summer of 1969 and the first presentation of the theory was given at the 18th Denver X-ray Conference (Sayers *et al.*, 1970). The theory had the basic ideas of the modern theory, except for the phase shift contribution of the back-scattering atoms. [This and multiple scatterings (MS) were added to the theory by Patrick A. Lee, whom I was fortunately able to attract to join the UW for the 1973–1974 academic year and to become interested in the theory of EXAFS.] Because of anticipated economic problems at Boeing, Dale was laid off and I placed him back on my grant to continue his thesis work.

By the end of the 1969–1970 academic year, the basic parts of the theory were essentially fully formulated, and I felt confident in Dale's mastery of it. In spite of the fact that our calculations of the photoelectron–atom interactions were crude, we had some success on materials with known structure to use the theory to fit their XAFS, but it was clear that the real pay-off would be to find a way to invert the process and apply EXAFS to determine the structure of unknown materials. Some details of the theory needed refinement and the experimental parts of the thesis needed completion, which Farrel Lytle was supervising. Dale was in the advanced stage where he could

complete his thesis without my close supervision, so I left on sabbatical leave to Israel for the 1970–1971 academic year, with instructions to Dale to concentrate on how to invert the theory to obtain structural information from the EXAFS data. We maintained frequent contact through correspondence by postal mail, which typically took a month for an exchange (e-mail did not exist then).

5. Fourier transform

In late 1970, Dale sent me a letter giving the final equation he had obtained for EXAFS after simplification. I quickly wrote back to him suggesting that Fourier transforming XAFS data should show peaks at the position of atoms. Dale performed such a transform on Ge data and, to our great excitement and satisfaction, the peaks appeared! Later, Farrel told me that Dale had also independently come to the idea of Fourier transforming the EXAFS data a few days before my letter had arrived. With this exciting result, we wrote a *Physical Review Letter* and submitted it for publication. The referee reports were mixed. One referee, who had obviously been involved in X-ray spectroscopy, considered the idea of the Fourier transform (FT) as trivial and not warranting a *Physical Review Letter*. Fortunately, our response, together with the positive referee reports were sufficient to convince the editor to publish our *Letter* (Sayers *et al.*, 1971).

Not only did we have the correct theory for EXAFS, but we also had the convincing evidence to prove it and a way to invert the XAFS data to determine unknown structures! The Fourier transform was the key to this. The fact that EXAFS was an SRO phenomenon was obvious, since the FT showed that all of the EXAFS signal came from the near neighborhood of the center atom (Figs. 1 and 2). The FT suggested how to overcome the major remaining theoretical obstacle to calculate correctly the photoelectron interaction with atoms. One

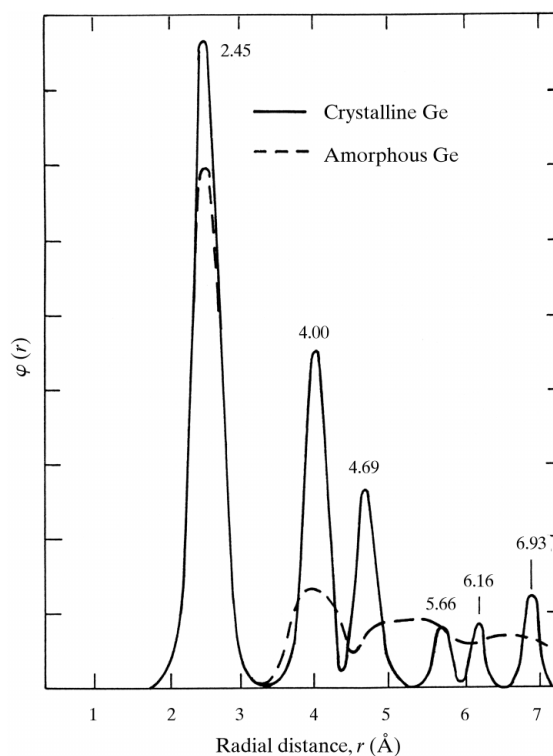


Figure 1 Magnitude of Fourier transforms of the EXAFS of crystalline (solid line) and amorphous (dashed line) Ge, as given in Sayers *et al.* (1971) using a laboratory X-ray spectrometer. The distance of the neighboring shells of atoms in crystalline Ge are given in Å.

did not have to perform such a calculation! Known structures can be used to obtain the information by measuring their EXAFS spectrum and then using the FT to isolate the signal from a given absorbing atom and its surrounding neighbor. This use of experimental standards was quite effective in the beginning to determine the structure of many materials and to prove its utility. The birth of the modern era of EXAFS as a quantitative structure-determination technique had arrived. A set of three papers summarized the theoretical, experimental and analysis status of our development of EXAFS up to 1974 (Stern, 1974; Lytle *et al.*, 1975; Stern *et al.*, 1975).

6. Synchrotron radiation

It should be noted that initially all EXAFS analysis of materials we made was based on measurements using Farrel's laboratory apparatus. Synchrotron radiation came on the scene later during a visit of Artie Bienenstock to the University of Washington to give a seminar. Artie told me about the exciting possibilities of using SPEAR, the Stanford University electron-positron collider at SLAC, for generation of X-rays from the synchrotron radiation that was a nuisance to the high-energy particle experimentalists. He convinced me to use this source of high-intensity X-rays to measure EXAFS. I subsequently testified at Artie's invitation to an NSF committee visiting SPEAR to evaluate the proposal from Stanford University to develop SPEAR as a high-intensity source of hard X-rays. The committee strongly encouraged me to go ahead and develop an XAFS beamline at SPEAR and, together with Peter Eisenberger, Brian Kincaid and Sally Hunter (the latter two being Artie's students), Dale, Farrel and I put together the first operating beamline

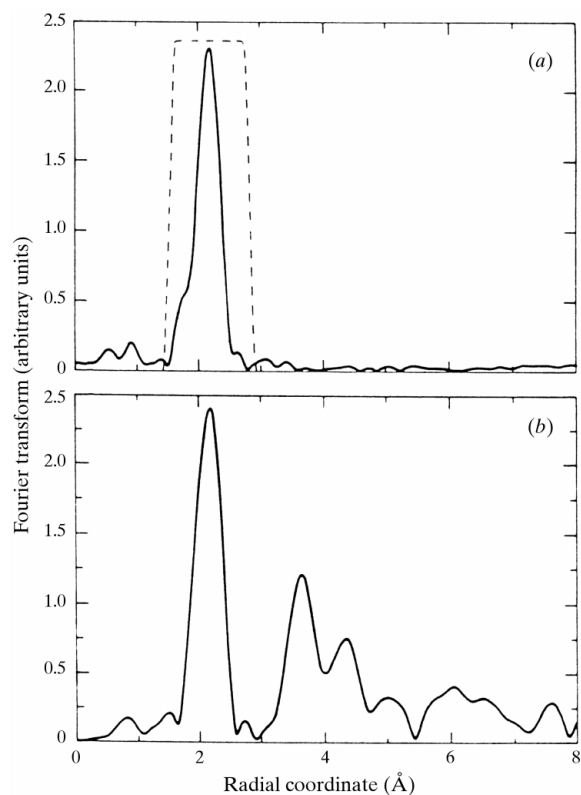


Figure 2

Similar data as in Fig. 1 are shown in a later investigation by Bouldin *et al.* (1984), showing improvements both in measuring capabilities using a synchrotron source and in analysis. Amorphous Ge with 4.9 at. % H is shown in (a), while crystalline Ge is shown in (b). In both (a) and (b) the transform range was $3\text{--}14 \text{ \AA}^{-1}$ and the XAFS was weighted by k^2 .

on the SPEAR machine at SSRP, the predecessor to SSRL (Eisenberger *et al.*, 1974).

As you all know, synchrotron radiation revolutionized the experimental side of EXAFS, making it accessible to non-experts and attracting the largest numbers of users at synchrotron sources. The revolution is best summarized by quoting from Lytle's article (1999): "In one trip to the synchrotron we collected more and better data in three days than in the previous ten years [with three laboratory X-ray spectrometers]".

7. Growing pains

As may be expected for a new technique that is not fully understood by new users, in the early days of the new era an exaggerated view of what EXAFS could accomplish was widely proclaimed by one new user. As he became more experienced in the technique and began to realise that his original optimism was misplaced, he became disillusioned, his opinion rebounded to the opposite extreme and the limitations of EXAFS were exaggerated in turn. In particular, interpretation of some of his EXAFS data, without taking into account systematic errors, led to an exaggerated estimate of the failure of chemical transferability of the amplitude function (Eisenberger & Lengeler, 1980). A more careful measurement of the chemical transferability of the amplitude function by our group found a much smaller variation (Stern *et al.*, 1980, 1981; Stern & Kim, 1981), confirming the suitability of using experimental standards. Unfortunately, the exaggerated image of the inaccuracies of EXAFS was reinforced by many other early users who overinterpreted their EXAFS data to draw wrong conclusions. This early history caused a delay in the acceptance of EXAFS among the general community, and we are still suffering its residue today. To counteract this trend, a workshop was convened on 7–9 March 1988 to start the effort to develop standards and criteria for XAFS (Lytle *et al.*, 1989). It could be argued that this was the final step towards the formation of the IXS which replaced the more informal organization that started in 1981 with the first international gathering of XAFS users organized by Samar Hasnain leading to the formation of an International Advisory Committee for continuing the XAFS conference series. The developing of standards and criteria is still continuing today, as will be presented later this morning. I want to emphasize the importance of assessment of uncertainties in the evaluation of structural parameters and the dominance in most cases of systematic uncertainties. It is, together with an educational effort to transmit these standards and criteria to the XAFS community, one of the most important things our community can do to repair our image and improve the reliability and quality of publications based on XAFS measurements.

I would like to emphasize one overinterpretation that is still all too common, namely overestimating the spatial resolution of XAFS. Similar to the Rayleigh criteria for resolving point sources, XAFS also has a criterion for resolving two distances and distinguishing their splitting, ΔR , from a Debye–Waller disorder, requiring the detection of a beat in k -space which leads to the result that $\Delta R \geq \pi/2k_m$, where k_m is the maximum wavenumber in the EXAFS data. For the typical case of oxygen as nearest neighbors, $k_m \leq 15 \text{ \AA}^{-1}$, giving the maximum spatial resolution of $\Delta R \geq 0.10 \text{ \AA}$. Any claim of a higher resolution of ΔR for two O atoms should be suspect.

8. Maturing

Our discipline has had an impressive advance in the capability to wring information from XAFS data since the days of experimental standards. The increased capability started with the theory of Lee &

Pendry (1975) that was the first reasonably quantitative theory for calculating EXAFS including MS. Subsequent contributions, as reviewed by Rehr in this conference (Rehr & Ankudinov, 2001), improved on the reliability of the theoretical calculation (Gurman *et al.*, 1986; McKale *et al.*, 1986; Binsted *et al.*, 1987; Filipponi *et al.*, 1991; Vedrinskii *et al.*, 1991; Filipponi & DiCicco, 1993; Binsted & Hasnain, 1996). In particular, the development of FEFF by Rehr and his collaborators (Rehr *et al.*, 1991; Zabinsky *et al.*, 1995; Ankudinov *et al.*, 1998) has produced a computer code that allows rapid calculations of the EXAFS spectra using only desktop computers. This allows experimentalists to combine theory with analysis computer routines, *e.g.* *UWXAFS* (Stern *et al.*, 1995), to rapidly refine structural fits to measured data and obtain reliable structures of samples. The *FEFF8* code of Ankudinov *et al.* (1998) allows a more accurate calculation of the X-ray absorption near-edge structure (XANES) by including self-consistent potentials taking into account full multiple scattering from atoms within a small cluster and the contribution of high-order multiple scattering from atoms outside the cluster. For many cases, such an impressive approach gives unprecedented agreement with experiment, but still not with the accuracy attained for EXAFS calculations. This reflects the more challenging physics problem associated with XANES. The interaction between the photoelectron, its ion core and neighboring atoms is much stronger relative to its kinetic energy than for EXAFS, where the interactions are weak compared with the kinetic energy. Effects that are negligible for EXAFS become important in the XANES. These include nonspherical corrections to the potentials, and many-body and core-hole interactions. For example, the XANES calculation of *FEFF8* are not adequate for solids where the electron–electron and electron–phonon interactions are so strong as to invalidate the Fermi liquid model for electrons, *e.g.* high- T_c superconductors. The challenge still remains to improve the theory for XANES further. The rewards of attaining such a theory for XANES justify the quest. In that case, XANES measurements may reveal new details about the electronic structure of solids with strong many-body interactions, such as high- T_c superconductors and colossal magnetoresistance, presently poorly understood phenomena.

On the experimental side, many developments have occurred allowing new capabilities of time and spatial resolution. I do not intend to discuss these because of lack of space, but I want to mention the opening of the field of magnetic XAFS due to experimental innovations (Schütz *et al.*, 1997). The ideas of XAFS have influenced and given birth to other techniques and phenomena, *e.g.* diffraction anomalous fine structure (DAFS) (Stragier *et al.*, 1992), photoelectron diffraction (Kaduwela *et al.*, 1991), various electron energy-loss techniques (Egerton, 1986) including extended energy-loss fine structure (EXELFS) (Stern *et al.*, 1994) and extended fine Auger structure (Chainet *et al.*, 1986), β -decay near threshold (Koonin, 1991), extended appearance potential fine structure (Mehl & Einstein, 1987), fine structure in isochromats (Fujimoto, 1965), photon interference XAFS (PIXAFS) (Nishino & Materlik, 1999; Nishino *et al.*, 2000) and the related X-ray ‘holography’ effects (Len *et al.*, 1997).

9. Retrospective

I feel most fortunate that circumstances converged to have me meet Farrel Lytle and be introduced to EXAFS whose theoretical understanding was delayed by 40 years due to an original theoretical confusion. I started my research on EXAFS purely out of scientific curiosity to understand it, without realising initially how powerful a structure-determination technique it would become. Only after

developing a theory that contained the essential physics did the realisation become apparent.

Yet, I am not a theorist but an experimentalist, who employs theory to devise new experiments to perform. In support of my experimental credentials I cite that an overwhelming number of my PhD students’ theses topics were experimental ones, and I have been intimately involved in developing experimental techniques for measuring XAFS, including the first such beamline at synchrotron sources and the Stern–Heald Soller-slit filter ion chamber fluorescence detector (Stern & Heald, 1979), which is now called the ‘Lytle’ detector after I gave him the plans of how to construct it. Fig. 3 is one of the few photographs I have of my laboratory that shows me and some of my then graduate students, *ca* 1983, in front of the laboratory XAFS facility I built in 1980. For comparison, Fig. 4 shows me at XAFS11 together with the Director of SPring-8 and a graduate student. Although my research in XAFS has been my most important scientific accomplishment, I have performed experiments and theory on other topics in condensed matter physics, some based on ideas that I believe are intellectually more clever than EXAFS, but they turned out to be less important.

In my case, luck has been an important factor in my scientific accomplishments, including the fact that I lived through the golden age of the 1950s and 1960s, when federal scientific funding was more plentiful and tolerant of basic research that had no obvious application nor followed the fads of the times. Without the federal support of my science from the US Air Force, NSF and DOE funding agencies, none of my research would have been possible and I am indebted to them and my monitors, especially Jerry Smith and Bill Oosterhuis of DOE.

10. Prospective

Synchrotron radiation sources have gone through three generations, each generation producing improved characteristics of X-rays so as to allow the further probing of the properties of matter with increased resolution in space, time and energy. There is a proposal for a new type of X-ray source whose feasibility is presently being explored,



Figure 3 Photograph *ca* 1983 taken in my laboratory with some of my then graduate students in front of the laboratory XAFS facility built in 1980. The facility is inside a lead-lined plywood enclosure and is hidden behind us. From left to right are: Ernest Janzen, Kyungha Kim, Grant Bunker, Edward A. Stern, Yves Idzerda.

which has been labelled the fourth-generation X-ray source. It employs a different mechanism for production of X-rays than that of the previous three generations, namely, free-electron laser amplification, similar to the free-electron laser for producing infrared radiation. Its X-rays are so much more brilliant than previously that they are as qualitatively different as a light bulb is to an optical laser. The X-ray free-electron laser, if it works as advertised, will have large numbers of coherent photons in a given mode, will consist of a train of pulses 230–100 fs in duration, large fluctuations in intensity between individual pulses and so intense that each pulse typically will destroy a condensed matter sample. All present synchrotron sources, in contrast, have a negligible probability of having more than one photon per mode, so that the interaction of different photons with matter is essentially incoherent.

Such a new source will open up qualitatively new physical phenomena, but at the same time will preclude the investigation of many of the phenomena presently being investigated.

It is my opinion that it is unjustified and misleading to call the XFEL a fourth-generation synchrotron source, just as it is unjustified to call the infrared free-electron laser a synchrotron source. It is not a synchrotron radiation source but an X-ray laser with a limited tunable range.

I cannot foresee in the near future, if ever, that the XFEL will be applicable to measuring XAFS because of the following: the extreme peak brilliance that destroys a sample in one pulse and excites atoms by multiple photons, causing a complicated superposition of mechanisms including non-linear effects within atoms; the requirement of an extremely fast detector that can count and energy-analyze many photons in the pulse duration; and to do this with an accuracy of 10^{-4} better when pulse-to-pulse variation is of the order of 10%.

The XAFS community must make it clear that the XFEL is not its fourth-generation synchrotron source, and I suspect that it also is not a fourth-generation source for many, if not all, of the present techniques being utilized currently at synchrotron sources. If we do not clarify this issue now, then the future funding of our present sources and real fourth-generation synchrotron sources may be jeopardized.

I want to emphasize that I am not against the building of the XFEL if its scientific case can be justified. However, it should be understood that the XFEL is *not* a fourth-generation synchrotron source but an exciting new type of source of X-rays that has the potential of

investigating completely new types of phenomenon and its case must be justified on that basis.

11. In gratitude and pride

XAFS graduate students: D. E. Sayers, M. Brown, B. Bunker, S. Csillag, J. Erskine, K. Kim, G. Bunker, C. E. Bouldin, K. Zhang, E. Keller, O. Pettitpierre, Y. Idzerda, Y. Ma, M. Qian, X. Li, J. Mustre de Leon, D. J. Thiel, Y. Zhang, M. Newville, D. Haskel, B. Ravel, B. Rechav, N. Sicon, M. VaarKamp, S. Kelly, V. S. Machavariani.

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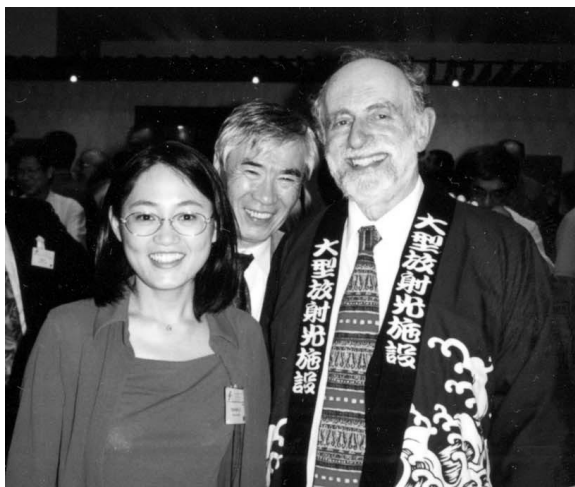


Figure 4

At XAFS11 during the SPring-8 reception. From left to right: Ms Kuniko Hayakawa, graduate student of Professor Fujikawa; Professor Hiromichi Kamitsubo, Director of SPring-8; and the author.

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