# Catching Phonons in Plutonium: My Story

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*It is an honor to contribute this invited article to celebrate the 20th anniversary issue of* Synchrotron Radiation News. *This is a story of how synchrotron radiation uniquely makes it possible for the determination of the phonon dispersions of Pu – a 40+-year problem not solvable with conventional inelastic neutron scattering and in the absence of large single-crystal specimens.*

In early 2002, I became curious about plutonium (Pu) science. I had never conducted any Pu research and wanted to see what new experiments could be done. After reading *Challenges in Pu Science* [1], I discovered that many articles in the two-volume compilation mentioned the importance of phonon dispersion curves (PDCs), yet no data had ever been collected on Pu PDCs.

Phonons, or lattice vibrations, are the acoustic equivalent of photons (the basic quanta of light). PDCs describe how atoms move within a solid and determine many physical properties, such as sound velocity, elasticity, and phase stability. These properties are highly anomalous in Pu, making the understanding of phonons key. The mechanisms behind Pu's phase stability are especially important because Pu exists in many different phases, undergoing crystallographic changes involving phonons each phase transformation.

I learned that despite 40+ years of attempts, two main obstacles had prevented the experimental determination of Pu's PDCs. First,

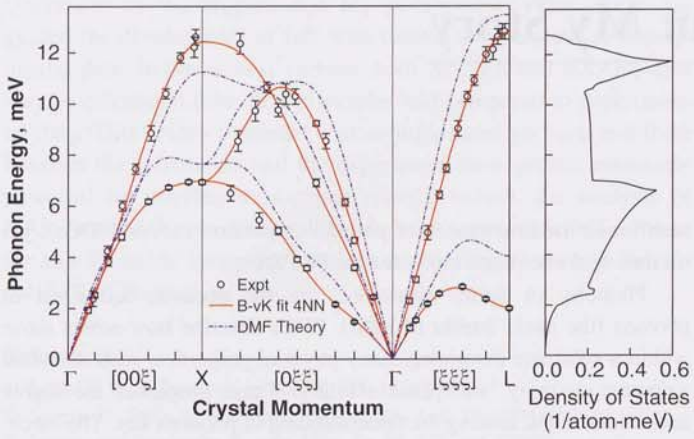


*Figure 1: Phonon dispersions along high symmetry directions on an fcc δ Pu-Ga alloy containing 2 at. % of Ga. The longitudinal and transverse modes are denoted L and T, respectively. The experimental data are shown as circles. Along the [0ξξ] direction, there are two transverse branches [011]<01-1> ($T_1$) and [011]<100> ($T_2$). Note the softening of the TA[ξξξ] branch toward the L point. The lattice parameter of our samples is a=0.4621 nanometer (nm). The solid red curves are the fourth-nearest neighbor Born-von Karman model fit. The IXS-derived phonon density of states, normalized to three states per atom, is plotted in the right panel. The dashed blue curves are calculated dispersions for pure δ-plutonium based on dynamical mean field theory (DMFT)[8].*

inelastic neutron scattering (INS), the leading method for measuring PDCs, requires single-crystal samples measuring at least 1 $cm^3$. However, Pu has repeatedly defied attempts to grow such crystals. Even if large Pu crystals were available, they would have to be made from a rare Pu isotope, $^{242}$Pu, because the other Pu isotopes tend to absorb neutron, thus stripping INS of its power.

To counter these obstacles, I conceived a *microbeam-on-single-grain* approach utilizing a recently developed technique called high-resolution inelastic X-ray scattering (HRIXS). HRIXS uses X-rays rather than neutrons, thereby avoiding Pu's neutron absorption problem. Moreover, small sample size is not an issue with HRIXS because it can use the ultrabright X-ray beams of third-generation synchrotrons, such as the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, to probe samples as small as $10^{-4}$ $mm^3$.

In February 2002, I traveled to ESRF and discussed the idea of using HRIXS to measure Pu phonons with Michael Krisch. Krisch, a phonon research expert who, with his colleagues, had developed and built a couple of HRIXS beamlines at ESRF for phonon dispersions research, was excited by the idea, and we began a cross-Atlantic collaboration.

I then applied for Feasibility Study funding from the Laboratory Science and Technology Operation (LSTO) office and was awarded a $75,000 grant in March 2002. Concurrently, I had also come across the pioneering thermal diffuse scattering (TDS) [2] to image phonons in crystalline solids by Tai Chiang's group at the University of Illinois at Urbana-Champaign (UIU). In May 2002, I visited his group at the Advanced Photon Source (APS) in Argonne, and discussed with M. Holt, H. Hong and P. Zschack the prospect of imaging phonons in Pu using TDS by totally containing a microbeam within a single grain of a polycrystalline specimen. This was also met with enthusiasm. In August 2002, we demonstrated the use of X-rays for imaging Pu phonons at the APS [3].

Having demonstrated the *microbeam-on-single-grain* concept, I succeeded in obtaining an additional funding from the LSTO office – this time a $500,000 exploratory research award. This grant funded our HRIXS experiments at ESRF, the only facility in the world that has both a high *enough* energy resolution ($10^{-7}$) and sensitivity (meV) needed to measure the phonon energies of Pu. Krisch and I were now joined by Dan Farber, Florent Occelli (then an LLNL postdoc, and now at CEA, France), and Adam Schwartz in the Pu IXS project.

Setting up the experiment at ESRF was extremely challenging. I had to fill out extensive paperwork to get authorization from both LLNL and ESRF for our experiment; ESRF beamtime (a scarce resource under high demand); and, above all, approval from French authorities to ship Pu samples to Grenoble [4]. Finally, in February 2003, our LLNL group traveled to France to work with M. Krisch at ESRF and began our first HRIXS measurements on Pu. The eight-day, round-the-clock run in February 2003 led to a successful mapping of the three longitudinal phonon branches in a δ Pu -2 at.%Ga fcc alloy, which has one atom per primitive cell. To map the remaining four transverse branches, however, a new design of the sample holder was needed to accommodate the transverse scattering geometry.

Fueled by the initial success and the knowledge that another group was attempting the same measurements at Argonne [5], my team returned to LLNL, redesigned the sample holder, made new Pu samples, filled out more paperwork to the French authorities for a new shipment to Grenoble, and requested a second beam time slot at ESRF. Amazingly, within a month we had accomplished all of these tasks and returned to ESRF on March 11, 2003, for another seven days of IXS measurements around the clock [6]. This time, we mapped all the four transverse branches, and obtained the first full phonon dispersions ever determined for any Pu-bearing material, catching a total of 58 phonons (Fig. 1).

Returning to Livermore, I collaborated with Tai Chiang in detailed analysis of the data. The preliminary Pu PDCs were presented in the 33rd *Journes des Actinides* conference in Prague, Czech Republic, at the end of April 2003. We submitted our first results to *Science* in late May, which were accepted (almost as is) in July and published in August 2003 [7]. In July, we presented a more complete analysis of the work at a conference on Pu Futures in Albuquerque. It was there we learned that our *Science* paper had been reviewed favorably by both G. Lander and G. Kotliar, who with his group from Rutgers University had calculated the PDCs for pure δ-Pu with

the dynamical mean field theory (DMFT) to include electron correlation effects. The theoretical results, which essentially contain all the qualitative aspects and semi-quantitative features of our IXS results, were calculated *without* any prior knowledge of our experimental data, but were held up somehow by *Science* for lack of comparison with experiments. In any event, the publication of the Rutgers' theoretical paper [8] in May 2003 led to ready acceptance of our IXS paper in July, and Lander was invited to write a perspective on our *Science* paper [9]. A detailed lattice dynamical analysis of our IXS results appeared later in a *Phys. Rev. B* paper [10].

My first (and only) venture into Pu research turned out to be my last and, perhaps, the most rewarding experiment in my career [11]—not only ending a 40+-year quest for the Pu phonons data since its discovery in 1941, but also opening the door to a new class of experimental research with micro-scale specimens. It is hoped that the current *microbeam-on single-grain* concept will soon be advanced, by the turn of the decade, to a *nanobeam-on single-grain* probe to further benefit both nano-scale R&D, which is flourishing, and actinide research where large single-crystal specimens are a rarity.

**Acknowledgments**

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**References**

1. *Challenges in Plutonium Science*, ed. by N.G. Cooper, Los Alamos Science, **26** (2006).
2. M. Holt, Z. Wu, H. Hong, P. Zschack, P. Jemian, J. Tischer, H. Chen and T.-C. Chiang, *Phys. Rev. Lett.* **83**, 3317 (1999); ibid, **86**, 3799 (2001).
3. Joe Wong, M. Wall, A.J. Schwartz, R. Xu, M. Holt, H. Hong, P. Zschack and T.-C. Chiang, *Appl. Phys. Lett.* **84**, 3747 (2004).
4. We came to learn that the last person to authorize (or otherwise) shipment of radioactive specimens was the pilot of the transporting airline carrier.
5. During our February 2003 run at ESRF, we were visited by both W. Stirling (ESRF Director General) and G. Lander (Director of the famous Institute of Transuranium Elements, Karlsruhe, Germany). Lander informed my group (I was doing the night shifts, sleeping in the daytime) on the experimental floor that he and other groups at both the APS and LANL were gearing up to measure the Pu PDCs at the APS, most likely that April. When I later visited the APS in October 2003 to deliver an invited seminar on our work, I learned that the APS-LANL- ITE experiment was suspended due to an earlier safety infraction of their earlier IXS experiment on uranium [M. E. Manley et al., *Phys Rev. B* **67**, 052302 (2003)].
6. On March 11, 2003, as we drove from Charles de Gaulle airport to Grenoble, we passed a red unmarked truck, which turned out to be transporting our 2nd set of specimens from Paris to Grenoble for our transverse phonons measurement. The truck had a breakdown en route, but got to ESRF a few hours before our run. It was that close!
7. Joe Wong, M. Krisch, D. Farber, F. Occelli, A. J. Schwartz, T.-C. Chiang, M. Wall and C. Boro, R. Xu, *Science* **301**, 1078 (2003).
8. X. Dai, S.Y. Savrasov, G. Hotliar, A. Migliori, H. Ledbetter, and E. Abrahams, *Science*, **300**, 953 (2003).
9. G. Lander also wrote a second perspective in *Physik Journal* [2 (2003) Nr. 11, 22], giving him two "papers" on Pu phonons.
10. Joe Wong, M. Krisch, D. Farber, F. Occelli, R. Xu, T.-C. Chiang, A. J. Schwartz, M. Wall and C. Boro, *Phys. Rev. B*, **72**, 064115 (2005).
11. For this work and some earlier EXAFS contributions, I was unexpectedly given an APS (American Physical Society) fellowship in 2005 – a very gratifying feeling for a physical chemist to go into retirement on March 1, 2006!

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