A First Look at Plutonium's Phonons

SINCE the discovery of plutonium in 1941, the element has both awed and perplexed scientists. The element's complexity and radioactivity have rendered it a challenge to study, but scientists persist because of the need to predict plutonium's behavior under various temperatures and pressure conditions and project how plutonium parts in weapons might change over time. Understanding the properties of plutonium is critical for the safe handling, use, and long-term storage of this material.

Livermore physical chemist Joe Wong is leading a team that has recently taken the first measurements of phonon dispersions in gallium-stabilized delta plutonium. This work sheds light on the movement of atoms in the crystal lattice of plutonium and provides a crucial piece in understanding the element's properties. The research is being conducted in collaboration with the European Synchrotron Radiation Facility in Grenoble, France, and the University of Illinois at Urbana–Champaign. The project is in its first year of funding from Livermore's Laboratory Directed Research and Development Program.

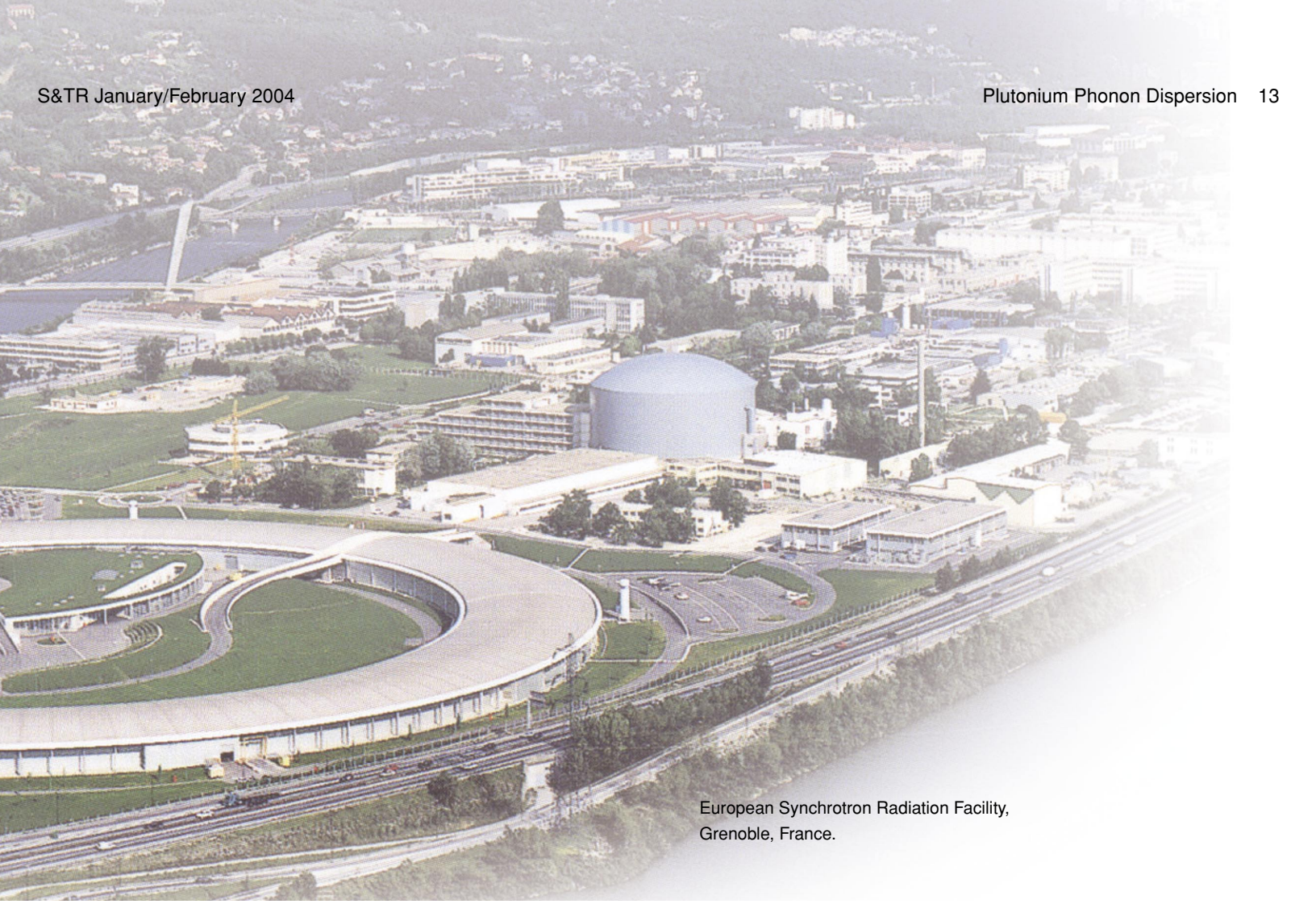
Phonons are lattice vibrations produced by the movement of atoms in a solid. Their variations along different crystallographic directions, called phonon dispersion curves (PDCs), describe how atoms move within a solid and are key to understanding many physical and structural properties, such as force constants, sound velocity, elasticity, heat capacity, and phase stability.

Plutonium and its alloys have defied phonon measurements for the past 40 years for several reasons. First, inelastic neutron scattering, the conventional method used to map phonon dispersions in most solids, requires large single crystals approximately a few millimeters in size, and it is not possible to grow plutonium crystals this large. Inelastic neutron scattering also would not work because of the high neutron absorption rate of plutonium—a quality that makes it ideal for nuclear weapons. Theoretical computations of plutonium's PDCs based on standard first-principles methods are difficult because of the complex correlating behavior of the element's electrons. Only recently has progress been made on the theoretical front to calculate the properties of plutonium. Thus, the PDCs for plutonium and its alloys have remained unknown experimentally and theoretically.

The element's complicated arrangement of 94 electrons contributes to its unpredictable behavior and difficulties in developing theories for plutonium's PDCs. As Wong explains, "If one is trying to make phonon predictions for systems with one or two electrons, it is quite easy. But when a system has 94 electrons, and many of them behave in any number of different ways, all bets are off." With most elements, electron behavior is relatively constant and predictable. However, in plutonium, the electrons are correlated. That is, what one electron does affects other electrons, and no adequate theories could predict those effects.

Plutonium's Peculiar Properties

On the periodic chart, plutonium sits halfway across the row of elements called actinides. The electrons on the outer shell of the elements in this row are progressively filled. The first few elements in the row are those whose electrons contribute to the bonding between atoms. Elements farther down the row, such as plutonium, have outer shells whose electrons may or may not participate in the bonding of atoms, and this variable leads to several unpredictable behaviors. Bonding or nonbonding behaviors are strongly reflected in the motions of the atoms in terms of the energy of the phonons

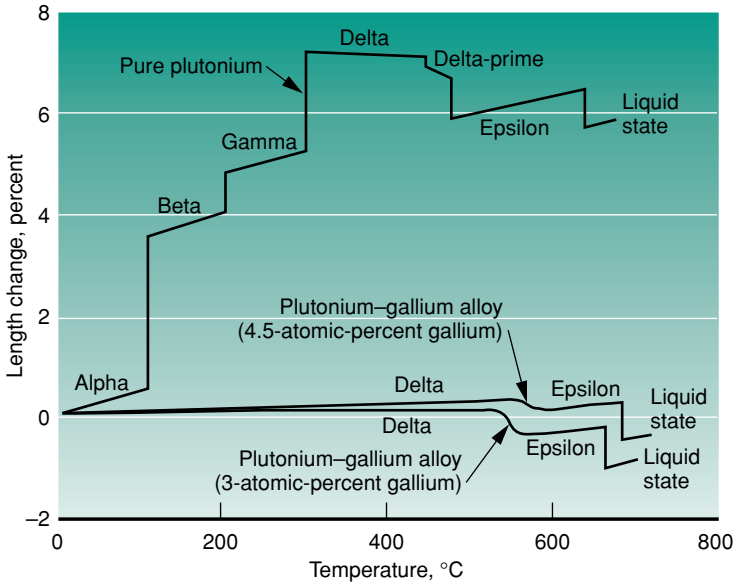


European Synchrotron Radiation Facility, Grenoble, France.

and their dispersion along various directions. Studying the phonon dispersions could answer some of the key questions scientists have about plutonium's behavior in its various phases and in different environments.

One of plutonium's unique physical properties is that the pure metal exhibits six solid-state phase transformations before reaching its liquid state, passing from alpha, beta, gamma, delta, delta-prime, to epsilon. Large volume expansions and contractions occur between the stable room-temperature alpha phase and the element's liquid state. Another unusual feature is that unalloyed plutonium melts at a relatively low temperature, approximately 640°C, to yield a liquid of higher density than the solid from which it melts. In addition, the elastic properties of the delta face-centered cubic (fcc) phase of plutonium are highly directional (anisotropic). That is, the elasticity of the metal varies widely along different crystallographic directions by as much as a factor of six to seven.

Wong's team focused on the delta fcc form of plutonium for phonon measurements because this form is stable at high temperatures and the highly symmetric fcc structure can be retained at room temperature by adding less than 2 atomic percent of an alloy metal such as gallium. For the initial feasibility study



Plutonium can be stabilized at room temperature by adding a small amount of a rare earth metal such as gallium.

and preliminary data analysis, Wong collaborated with physics professor T. C. Chiang at the University of Illinois.

To overcome the obstacles presented with the inelastic neutron scattering method, Wong worked with physicist Michael Krisch at the European Synchrotron Radiation Facility, which has a high-resolution inelastic x-ray scattering (HRIXS) beamline suitable for measuring phonons in plutonium. HRIXS's extremely bright x-ray sources and high-performance focusing optics enable researchers to conduct experiments on materials that are available only in small quantities. For many of the actinide elements such as plutonium, the sample volume is as small as one ten-thousandth of a cubic millimeter.

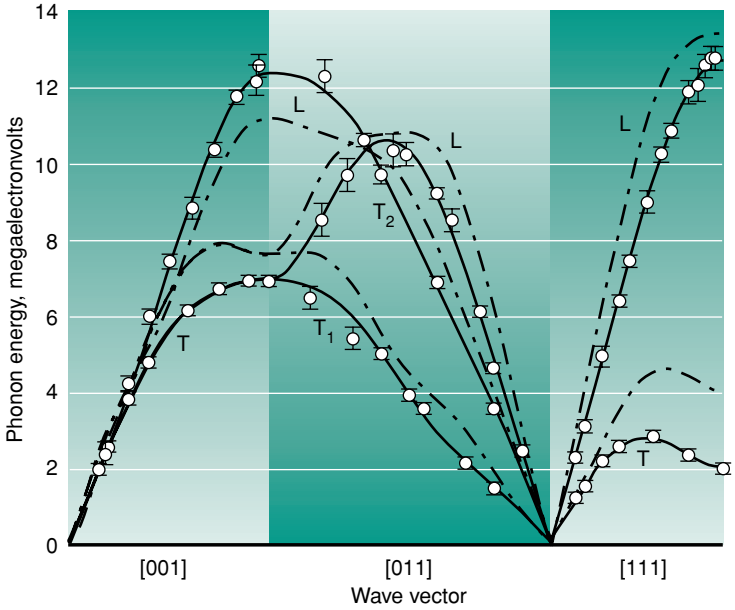
Mapping Phonon Dispersion Curves

Researchers directed a high-energy (21-kiloelectronvolt), high-brightness x-ray microbeam measuring 30 by 60 micrometers onto a single grain in large-grain polycrystalline specimens, each 10 micrometers thick. The specimens were prepared from a plutonium–gallium alloy containing approximately 2-atomic-percent gallium. Single-crystal domains of the fcc delta-plutonium were selected. The phonon energy was then measured and mapped along the three principal directions as a function of the scattering angle, which determined the wave vector of phonon propagation. When the motion of the atoms is along the same direction as the phonon wave propagation, a longitudinal (L) mode is produced. When the motion of the atoms is at a right angle to the phonon wave propagation, a transverse (T) mode is produced.

Scientists can interpret property characteristics from these phonon dispersions. For instance, they observed a profound elastic anisotropy in plutonium, more than in any other fcc metal known. Data also showed that the T [111] mode exhibits a pronounced bending along the transverse branch. Wong and his colleagues believe these features can be related to the phase transformations of plutonium and to the strong coupling between the vibrational structure and the electron instabilities on plutonium's outer electronic shell.

The resulting dispersion values generally agreed with the theoretical calculations based on recent dynamical mean field theory results. The theory incorporates correlation effects among plutonium's electrons and calculates phonon spectra at arbitrary wavelengths.

The experiments confirmed that recent theories explaining plutonium's phonon dispersions have been on the right track. However, a few quantitative differences warrant further study. Laboratory physicists Dan Farber and Florent Occelli and metallurgist Adam Schwartz are collaborating with Wong to gather more data. The team is interested in studying the effects of combining different amounts of gallium with plutonium and in determining how the phonon behavior affects the stability of the various chemical and structural phases of plutonium.



Phonon dispersions along the principal crystallographic directions [001, 011, 111] in a plutonium–gallium alloy. The longitudal and transverse wave vectors are denoted by L and T, respectively. The experimental data are shown as circles. The solid lines are the data's fits to the Born–von Karman model of lattice dynamics. The dashed lines are theoretically calculated dispersions for pure delta-plutonium based on the recent dynamical mean field theory.

Wong says, "These results not only add knowledge to our understanding of the properties of plutonium but also give us real data to test the existing theories and gain more confidence in those theories. We want to continue to gain scientific insight into plutonium's behavior in various environments, so we can contribute to the success of the Laboratory's science-based stockpile stewardship mission."

—Gabriele Rennie

Key Words: actinides, dynamical mean field theory, gallium, phonon dispersion curve (PDC), plutonium.

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