ficient thermal energy, leading to a different STP (*27*). Similar temperature-dependent behavior has been reported in previous transport measurements on tolane molecules (*28*). To this end, the conjugated molecule acts as a "quantum information bus" at room temperature.

These spin-transfer measurements on chemically synthesized QD systems bridged by conjugated molecules have important implications and open exciting opportunities on several fronts. The data indicate that small conjugated molecules can serve as natural media for shuttling quantum information and represent a step toward a bottom-up paradigm for spintronics manufacturing. Different conjugated molecules and QDs should provide additional insight into the proposed π-orbital–mediated spin interaction mechanism and help to define multifunctional magnetoelectronic elements. By electrically gating the molecules to manipulate the molecular conformations or by using optical pulses to excite the vibration modes of connecting molecules, chemically synthesized devices and scalable assembly may lead to room-temperature systems for quantum information processing (*1*).

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12. Several techniques were applied to characterize our samples. Atomic force microscopy (AFM) (Nanoscope III, Veeco Instruments) was used to characterize the topography of samples immediately after assembly. The images show high density and uniform coverage of CdSe QDs on the fused silica substrate over a large (micrometer) scale (Fig. 1B, inset). Formation of multilayer structures is further confirmed with the observation of a steady increase of optical density as the number of assembled layers increased consecutively.
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18. Theoretical molecular lengths of TOPO and 1,4-benzenedimethanethiol are ~1.1 and ~0.8 nm, respectively. In real samples, however, these molecules may be stretched or compressed. In addition, because TOPO ligands are longer than 1,4-benzenedimethanethiol, the cross-linkages of lateral QDs are very unlikely.
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27. We emphasize that a molecule in a self-assembled structure should have different conformational energetics compared with a molecule in either solution or crystal. For example, the QD-sulfur bonds as well as the intermolecular spacing should put constraints on molecular orientations. Our molecular simulations further suggest that the transition and the saturation behavior of STP result from the collective motion of neighboring molecules due to the molecule-molecule interactions and closely packed structures in samples (*29*). In addition, although this model uses dynamic wave function coupling between QDs through conjugated molecular π-orbitals, this mechanism may be related to the discussion of superexchange in supramolecular structures.
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Phonon Dispersions of fcc δ-Plutonium-Gallium by Inelastic X-ray Scattering

Joe Wong,[1]* Michael Krisch,[2] Daniel L. Farber,[1] Florent Occelli,[1] Adam J. Schwartz,[1] Tai-C. Chiang,[3] Mark Wall,[1] Carl Boro,[1] Ruqing Xu[3]

We report an experimental determination of the phonon dispersion curves in a face-centered cubic (fcc) δ-plutonium–0.6 weight % gallium alloy. Several unusual features, including a large elastic anisotropy, a small-shear elastic modulus C', a Kohn-like anomaly in the $T_1[011]$ branch, and a pronounced softening of the [111] transverse modes, are found. These features can be related to the phase transitions of plutonium and to strong coupling between the lattice structure and the 5f valence instabilities. Our results also provide a critical test for theoretical treatments of highly correlated 5f electron systems as exemplified by recent dynamical mean field theory calculations for δ-plutonium.

Plutonium (Pu) is arguably the most complex metallic element known and has attracted extraordinary scientific interest since its discovery in 1941. Further, detailed understanding of the properties of Pu and its alloys is critical for the safe handling, use, and long-term storage of these important, but highly toxic, materials. However, both technical and safety issues have made experimental observations extremely difficult. Pu is well known to have complex and often unique physical properties (*1*, *2*). Notably, the pure metal exhibits six solid-state phase transformations with large volume expansions and contractions between the room-temperature stable α-phase and the liquid state: $\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \delta \rightarrow \delta' \rightarrow \varepsilon \rightarrow$ liquid. Furthermore, unalloyed Pu melts at a relatively low temperature, ~640°C, to yield a liquid of higher density than the solid from which it melts. The face-centered cubic (fcc) δ-phase with density $\sim$15.92 g/cm^3 is ~20% lower in density than the monoclinic α-phase (19.86 g/cm^3). Pu can be retained in the highly symmetric fcc structure at room temperature by alloying with small amounts of Group III metals such as aluminum (Al) or gallium (Ga). In doing so, the metastable δ-phase field is expanded from high tem-

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[1] Lawrence Livermore National Laboratory, University of California, Post Office Box 808, Livermore, CA 94551, USA. [2] European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France. [3] Department of Physics and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana–Champaign, 1110 West Green Street, Urbana, IL 61801, USA.

*To whom correspondence should be addressed. E-mail: wong10@llnl.gov

perature to room temperature and below at the expense of the γ and β phases (*3*, *4*), suggesting very similar ground-state energies for these structures (*5*). Understanding the physical basis for the intriguing properties of Pu materials such as force constants, sound velocities, elasticity, phase stability, and thermodynamic properties critically hinges on the ability to produce high-quality experimental data. Of these, phonon dispersion curves (PDCs) are key to the elucidation of many of these physical phenomena. However, PDCs in Pu and its alloys have defied experimental determinations for the past 40 years because of both the inability to grow the large single crystals (a few mm^3) necessary for inelastic neutron scattering (INS) measurements and the high thermal-neutron absorption cross section of the most common isotope, ^{239}Pu. Further, only recently (*6*) have theoretical computations of the Pu PDCs begun to overcome the difficulties in treating the f electrons accurately within the standard first-principles methods. Thus, the PDCs for Pu-bearing systems have remained essentially unknown experimentally and theoretically.

The experimental difficulties associated with INS are circumvented in the present work by use of inelastic x-ray scattering (IXS) with meV energy resolution (*7*). With the advent of highly brilliant x-ray sources and high-performance focusing optics, samples with volumes as small as 10^{-4} mm^3 can now be studied (*8*, *9*). These capabilities have opened up new experimental opportunities for materials that are only available in small quantities, as is the case for many actinide systems (*10*).

Our samples were large-grain polycrystalline specimens prepared from a Pu-Ga alloy containing ~0.6 weight % Ga produced by a strain-enhanced recrystallization technique (*11*). Typical IXS spectra (Fig. 1) are shown for longitudinal acoustic (LA) and transverse acoustic (TA) phonons along the [111] direction at the selected reduced momentum transfer ($\xi\xi\xi$). The spectra (*12*) are characterized by an elastic contribution centered at zero energy and two inelastic contributions, corresponding to the creation (energy loss, Stokes) and annihilation (energy gain, anti-Stokes) of an acoustic phonon. To extract the phonon energies, the spectra were fitted by convolving the experimentally determined resolution profile with a model function consisting of a Lorentzian for the elastic contribution and a pair of Lorentzians, constrained by the thermal phonon population factor, for the inelastic part. The resulting PDCs along the three principal symmetry directions in the fcc lattice are displayed in Fig. 2, together with a fit obtained by means of a standard Born–von Kármán (B-vK) force constant model (*13*). An adequate fit to the experimental data is obtained if interactions up to the fourth-nearest neighbors are included, and the calculated phonon density of states derived from the B-vK model is also shown. The dashed curves are recent DMFT (dynamical mean field theory) results by Dai *et al.* (*6*).

The elastic moduli calculated from the slopes of the experimental PDCs near the Γ point (i.e., center of the Brillcuin zone) are $C_{11} = 35.3 \pm 1.4$ GPa, $C_{12} = 25.5 \pm 1.5$ GPa, and $C_{44} = 30.53 \pm 1.1$ GPa. These values are in excellent agreement with those of the only other measurement on a similar alloy (1 weight % Ga) obtained with ultrasonic techniques (*14*), as well as with those recently calculated from a combined DMFT and linear response theory for pure δ-Pu (*6*). The small difference between C_{11} and C_{44} is very unusual for an fcc metal. The shear moduli C_{44} and $C' = (C_{11} - C_{12})/2$ differ by a factor of 6. This is in contrast to that of a "normal" fcc metal such as aluminum (1.2) (*15*) and is much higher than values in other "unusual" fcc metals such as γ-Ce (2.8) (*16*, *17*), La (4.1) (*18*), and Th (3.6) (*19*). These results support the conclusion that δ-Pu-Ga is the most elastically anisotropic fcc metal known (*14*). Furthermore, we observe a large deviation, Δ, from the Cauchy criterion (*13*). Our measurement yields $\Delta = (C_{44} - C_{12})/C_{12} = 0.9$, which is nonzero and implies that the interatomic forces have a strong noncentral component.

The measured PDCs display several other unusual features. The T_1 branch along [011] exhibits a "kink," suggesting a Kohn anomaly similar to that observed in the light actinide Th (*19*). By analogy with all other phonon anomalies observed in metals, this is likely caused by electronic effects. Because the sound velocity of this mode is given by $\sqrt{C'/\rho}$ (where ρ is the density), it is clear that this anomaly is directly responsible for the suppression of C' and implies a soft response of the system to volume-conserving tetragonal distortion. This may explain the high-temperature phase transitions of Pu from δ to δ' (body-centered tetragonal) and to ε (body-centered cubic), which involve just this type of tetragonal distortion via the so-called Bain path. Although the Kohn-like anomaly suggests that the fundamental mechanism for the transition arises from electron-phonon interactions, it has been suggested (*6*) that the details of the transition further involve anharmonicity and phonon entropy.

The most pronounced feature of the experimental PDCs is a soft-mode behavior for the TA branch along [111]. A similar feature (but occurring at about twice the energy and at a higher crystal momentum toward the L point) is also seen in a recent DMFT calculation for δ-Pu (*6*). The cubic fcc crystal structure of δ-Pu can be viewed as being composed of hexagonally close-

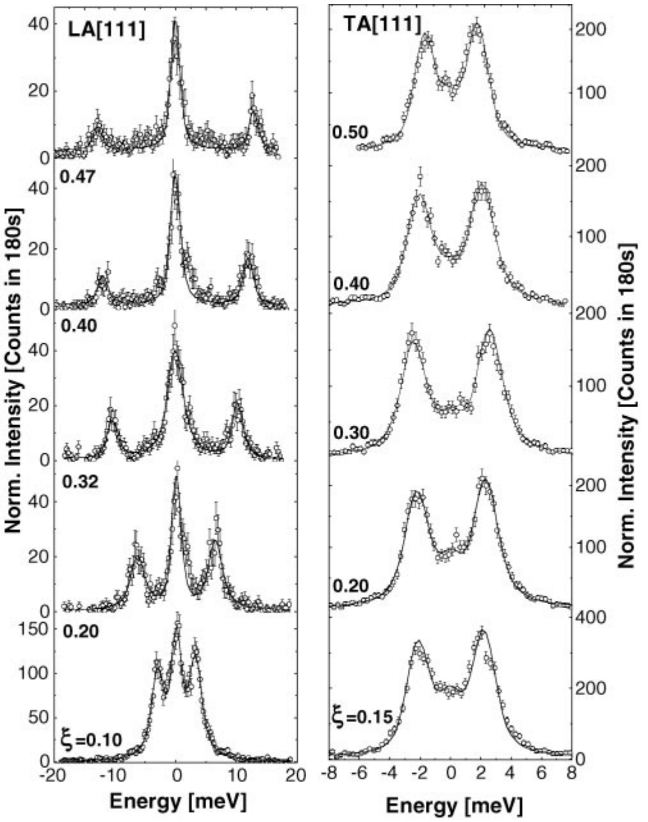

Fig. 1. Representative IXS spectra for the longitudinal acoustic (LA) and the transverse acoustic (TA) phonon branches along [111] in a δ-Pu–0.6 weight % Ga alloy. The experimental data are shown together with the results of the best-fit model of the phonon and elastic contributions. The corresponding reduced phonon wave vectors, ξ, are indicated to the left of the spectra.

packed atomic planes stacked along the [111] direction with a specific stacking arrangement. The soft transverse mode at L suggests that each atomic plane could easily slide relative to its immediate neighboring atomic planes to form new stacking arrangements. Pure δ-Pu, on lowering temperature, transforms into the γ phase, which has a face-centered orthorhombic structure (*20*). This structure can be described in terms of a stack of slightly distorted hexagonally packed atomic layers and indeed is the type of structure that could be easily obtained by layer parallel shear in the fcc phase. Thus, the soft mode at L is likely a key feature associated with the δ to γ transition, even though this transition is suppressed by Ga stabilization in the present case (*21*). This notion is indeed substantiated by the fact that the first interplanar force constant (derived from the B-vK model) of the T[111] mode is more than an order of magnitude smaller than those of the transverse modes in the other two directions. The small amount of Ga in the sample is sufficient to allow the system to bypass the γ and β phases and make a transition directly to a monoclinic α′ phase at about −110°C. The α′ phase (*22*), despite its apparent complexity, is also a slightly distorted hexagonal close-packed structure and is easily accessible from the fcc phase through the same shear mechanism. A similar soft-mode behavior has been observed in γ-Ce (*16*, *17*) and La (*18*). In those cases, the transition leads, instead, to a double-hexagonal close-packed structure, but the same general concept of layer parallel shear applies.

Pu sits in a unique position within the actinide series between elements with itinerant (bonding) or localized (nonbonding) 5f electrons (*1*, *3*). The different polymorphs of Pu have 5f electrons that span the range between itinerant or localized behavior. The exact nature of the 5f electrons in Pu is extremely sensitive to changes in intensive parameters such as temperature, pressure (*23*), and chemical potential (alloying) (*23*). In general, anomalies in PDCs such as those we document here in δ-Pu-Ga are derived from electronic interactions, and some of the same anomalies were previously known in other actinide systems. This suggests that the 5f electronic structure is the underlying cause for these anomalies. Furthermore, valence instability in the 5f electronic structure, together with strong electron-phonon coupling, is likely the underlying reason for both the phonon anomalies we observe and the rich variety of polymorphic phase transitions present in this exotic material.

As evident in Fig. 2, the present IXS experiment validates the main qualitative predictions of a recent DMFT calculation for δ-Pu (*6*) in terms of (i) a low-shear elastic modulus C′, (ii) a Kohn-like anomaly in the T1[011] branch, and (iii) a large softening of the T[111] modes. Such experimental-theoretical agreements give credence to the DMFT approach for the theoretical treatment of 5f electron systems, of which Pu is a classic example. However, although there is good qualitative agreement between theory and experiment, quantitative differences indeed exist. These are (i) the position of the Kohn anomaly along the T_1[011] branch, (ii) the energy maximum of the T[111] modes, and (iii) the softening of the calculated T[100] branch near the X point, which is not observed experimentally. These differences are real and thus provide the framework for refined theoretical treatments and further experiments in Pu and other 5f systems.

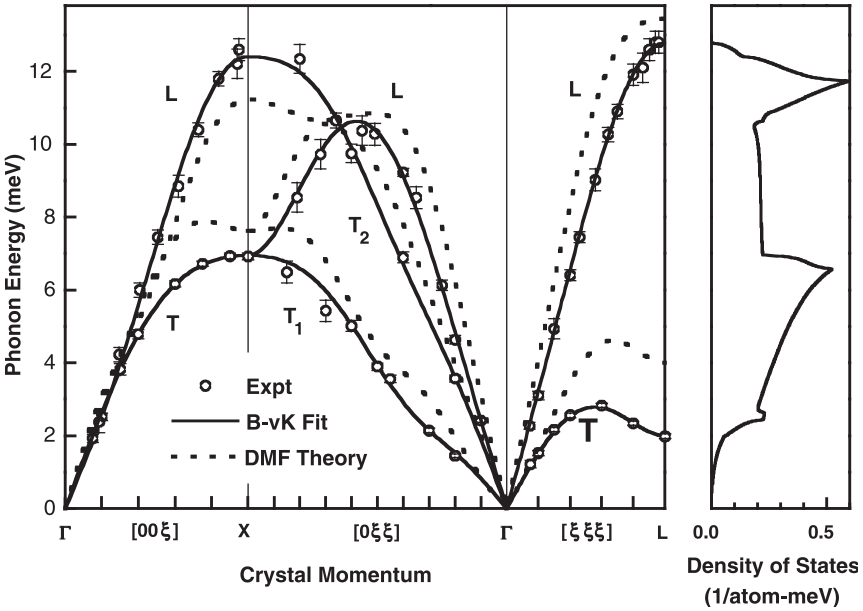

Fig. 2. Phonon dispersions along high-symmetry directions in δ-Pu–0.6 weight % Ga alloy. The longitudinal and transverse modes are denoted L and T, respectively. The experimental data are shown as circles. Along the [0ξξ] direction, there are two transverse branches, [011]⟨011⟩ (T_1) and [011]⟨100⟩ (T_2). The softening of the TA[111] branch toward the L point is apparent. The lattice parameter of our samples is *a* = 0.4621 nm. The solid curves are the fourth-nearest neighbor Born–von Kármán (B-vK) model fit. The derived phonon density of states, normalized to three states per atom, is plotted in the right panel. The dashed curves are calculated dispersions for pure δ-Pu based on DMFT (*6*).

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