Symmetry and Stability of δ Plutonium: The Influence of Electronic Structure

K. T. Moore,[1,*] P. Söderlind,[1] A. J. Schwartz,[1] and D. E. Laughlin[2]
[1]*Lawrence Livermore National Laboratory, Livermore, California 94550, USA*
[2]*Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213 USA*
(Received 27 September 2005; published 26 May 2006)

Using first-principles density-functional theory, we calculate the bond strengths between the 12 nearest neighbors in δ plutonium for both pure Pu and a Pu-3.7 at. % Ga alloy. Our results for pure Pu reveal a structure with the monoclinic space group Cm rather than face-centered cubic $Fm\bar{3}m$, showing that the anomalously large anisotropy of δ plutonium is a consequence of greatly varying bond strengths between the 12 nearest neighbors. Further results for a Pu-3.7 at. % Ga alloy show that the nearest-neighbor bond strengths around a Ga atom are more uniform. Hence, our calculations address (i) why the ground state of Pu is monoclinic, (ii) why distortions of the δ phase are viable, with considerable implications for the behavior of the material as it ages due to anisotropic response to self-irradiation, and (iii) why Ga stabilizes face-centered cubic δ-Pu.

DOI: 10.1103/PhysRevLett.96.206402 PACS numbers: 71.20.Gj, 71.15.Mb, 71.27.+a, 71.28.+d

Classical crystallography does not incorporate anisotropy of atomic bonds within its framework; rather, it assumes a spherical atom occupies each lattice site [1]. While this assumption is justifiable for some elements, it becomes less reliable for those with complicated electronic structures. Nowhere is this more apparent than for plutonium, which is the most enigmatic metal in the periodic table [2–8]. Recently, the phonon dispersion curves for single-grain δ plutonium were recorded using inelastic x-ray scattering [9], confirming other measurements [10,11] that it is the most anisotropic face-centered cubic (fcc) metal known. The shear moduli C_{44} and C' differ by a factor of ~7, which is in strong contrast to aluminum exhibiting a factor of 1.2 [12]. In addition, δ-Pu has a negative coefficient of thermal expansion and has the most crystallographically expanded lattice of all six Pu allotropes (fcc is usually the most densely packed crystal structure). This is evidence that a simple hard-sphere assumption is inappropriate for Pu and that the bonding strengths between the 12 nearest neighbors of the fcc δ-Pu lattice are not equal. In turn, this means that the total symmetry of the metal may not be fcc but rather a lower-symmetry class.

Here we present a novel use of first-principles calculations, which yields the bond strengths of the 12 nearest neighbors within the δ-Pu crystal of both pure Pu and a Pu-3.7 at. % Ga alloy. Using these calculated bond strengths, we systematically progress through crystallographic arguments, showing that the δ phase of pure Pu belongs to the monoclinic space group Cm rather than the cubic $Fm\bar{3}m$ space group. Our results provide new insight into why plutonium is the only metal with a monoclinic ground state and why tetragonal, orthorhombic, or monoclinic distortions of δ-Pu are likely. These distortions have considerable ramifications for the behavior of the metal as it ages, accumulating damage via self-irradiation. We also present results for a Pu-3.7 at. % Ga alloy that show that the bond strengths around the Ga atom are more uniform than for a Pu atom surrounded by other Pu atoms, a result that illuminates why Ga acts to stabilize the fcc δ phase over the monoclinic α phase.

Let us begin with a two-dimensional array of blocks, as shown in Figs. 1(a) and 1(b). First, a square array of points is created, which is the *lattice*. Blocks are then incorporated around each lattice point, which is the *motif*. The resulting structure is shown Fig. 1(a). The combination of a lattice and motif in two dimensions results in a *plane group*, the two-dimensional analog to a *space group* for three dimensions. This two-dimensional structure in Fig. 1(a) has a plane group symmetry of $4mm$, because there is an axis of fourfold rotation about each lattice point and there are four mirror planes marked m_1, m_2, m_3, and m_4. When the upper-left and lower-right corners of each block are filled, the motif is altered. The plane group symmetry of this structure is accordingly reduced to $2mm$ because of the loss of fourfold symmetry and the elimination of the m_1 and m_2 mirror plane planes. The

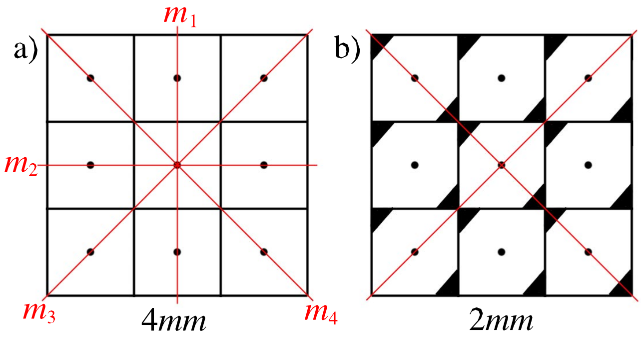

FIG. 1 (color online). Two periodic arrays illustrating repetition of a lattice (points) and a motif (blocks). (a) A pattern showing a plane group symmetry of $4mm$ and (b) a pattern showing a plane group symmetry of $2mm$, reduced only by a change in the motif, not the lattice.

important point here is that the structure in Fig. 1(b) still has a square lattice, even though the axis of fourfold symmetry is lost and the total symmetry of the structure is reduced.

An example of this idea in three dimensions and in a real crystal is the body-centered cubic (bcc) structure of α-iron. When paramagnetic, the structure has a bcc space group of $Im\bar{3}m$. However, when the crystal structure becomes ferromagnetic with aligned moments in the [001] direction, the symmetry is reduced to $I4/mm'm'$, as shown in Fig. 2 [13]. From a geometry standpoint, $a = b = c$, but the fact that the spins are aligned along the z axis lowers the symmetry of the crystal structure. Thus, there do not need to be atomic displacements, and, correspondingly, a change in lattice, to reduce the total symmetry of the structure.

In the case of the two-dimensional array of blocks in Fig. 1 (plane group) or in the three-dimensional bcc structure of α-iron (space group), the same point comes out: The lattice itself may remain high symmetry, but the crystal structure as a whole may be reduced in symmetry due to a change in motif. This is because the symmetry of any plane or space group is composed of the intersection of the symmetries of a lattice and a motif. In ferromagnetic α-iron, the magnetic moment produced by the outermost valence electrons not only degrades the symmetry from bcc to tetragonal but also alters the macroscopic properties that we observe, such as elastic constants, shear modulus, and phase transformations. While a magnetic moment can reduce symmetry as described above, other aspects of the outermost bonding electrons can also affect the symmetry.

Armed with this knowledge, let us return to the case of δ-Pu. We begin with the assumption that the lattice is fcc with $a = b = c$. A motif is then created, which is the bond strengths for the 12 nearest neighbors. The question is if an fcc lattice is joined with a motif of anisotropic bonds, what is the resultant space group? In order to resolve this issue, the detailed electronic structure of Pu must be determined and, in particular, the variation of the nearest-neighbor bond strengths. By calculating the energy response (ΔE) of a ~2% (0.049 Å) displacement of an atom along each of the 12 nearest-neighbor directions, an approximate force or strength of the bonds is realized. This energy response or force F (mRy/Å) is the "bond strength." These energies are obtained from first-principles electronic-structure calculations within the framework of density-functional theory (DFT). This approach has proven to be remarkably accurate for Pu [14], whose electron-correlation effects and their origin are still debated. Regardless of the exact mechanisms, spin-polarized DFT approximates the energies of these correlations well. The computational details are similar to those in Ref. [14], with the major difference being that here we study a 27-atom supercell of fcc Pu to allow for the above-mentioned atomic displacements. To simplify the calculations, the effect of electron spin is only accounted for by a parallel arrangement and not coupled to the orbital degree of freedom. This assumption is believed to be valid, because most of the polarization effects are captured by the spin degree of freedom, and the ferromagnetic arrangement gives very similar equilibrium volume, bulk modulus, elastic constants, and thus overall chemical bonding as the preferred disordered state [15].

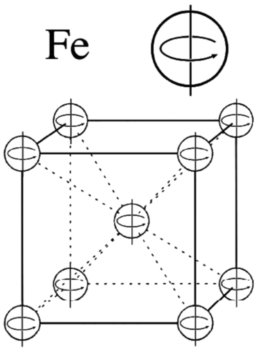

FIG. 2. The structure of α-iron. The crystal has a body-centered cubic space group of $Im\bar{3}m$ when paramagnetic but is reduced to $I4/mm'm'$ when the crystal becomes ferromagnetic with aligned moments in the [001] direction.

The results of the calculations for pure Pu are shown in Table I and Fig. 3. The nearest-neighbor direction (x, y, z), Miller indices (h, k, l), and bond strength F (mRy/Å) due to the change in energy resulting from a 2% shift of the 0, 0, 0 atom are shown in Table I. Notice how F varies from ~3.3 to ~5.3 for pure Pu, showing the large degree of variation in bond strength between the 12 nearest neighbors. As shown in Fig. 3, the 12 nearest neighbors can be separated into six pairs of two where the bond strengths are close in value: blue (3.3), black (3.5–3.7), red (3.7–3.9), pink (3.9–4.1), green (4.5–4.7), and brown (4.7–5.3). In the (001) plane, the [110] bond is roughly equal to the $[\bar{1}\,\bar{1}\,0]$ bond (green), and the $[\bar{1}10]$ bond is roughly equal to the $[1\bar{1}0]$ bond (black). In the {011} planes, we see that $[01\bar{1}] \sim [\bar{1}0\bar{1}]$ (blue), $[0\bar{1}\,\bar{1}] \sim [10\bar{1}]$ (red), $[0\bar{1}1] \sim [101]$ (pink), and $[011] \sim [\bar{1}01]$ (brown). It is important to note that not only the bond strength but also the repeatability of groupings dictate the choice of sets. In other words, there is a clear separation between the brown and pink sets and a clear separation between the red and blue sets. It is interesting that the bonds in the (001) plane are almost equal directly across the central atom, whereas the bonds in the {011} planes are not and have a more complicated arrangement.

When an fcc lattice is joined with the calculated bond strengths as a motif, the resultant structure is c-centered monoclinic with the space group Cm. This low-symmetry space group is due to the fact that, besides translational symmetry, there is no rotational symmetry and only one mirror plane along the (110) plane. This space group has several ramifications. First, it now seems no coincidence that the ground state α phase of Pu is monoclinic $P2_1/m$ and that here we show δ-Pu exhibits a monoclinic space group when the bonding strengths are accounted for as the

TABLE I. The nearest-neighbor direction in (x, y, z) coordinates, Miller indices (h, k, l), and bond strength F (mRy/Å) for pure Pu and a gallium atom in a Pu-3.7 at. % Ga alloy.

Nearest neighbor (x, y, z)	Miller indices (h, k, l)	Pure Pu F (mRy/Å)	Pu-3.7 at. % Ga F (mRy/Å)
0.5, 0.5, 0	1, 1, 0	4.7	6.3
−0.5, −0.5, 0	−1, −1, 0	4.5	6.1
0.5, −0.5, 0	1, −1, 0	3.7	6.3
−0.5, 0.5, 0	−1, 1, 0	3.5	6.4
0.5, 0, 0.5	1, 0, 1	4.1	7.0
−0.5, 0, −0.5	−1, 0, −1	3.3	5.6
−0.5, 0, 0.5	−1, 0, 1	4.7	4.4
0.5, 0, −0.5	1, 0, −1	3.9	5.5
0, −0.5, 0.5	0, −1, 1	3.9	7.3
0, 0.5, −0.5	0, 1, −1	3.3	5.9
0, 0.5, 0.5	0, 1, 1	5.3	6.0
0, −0.5, −0.5	0, −1, −1	3.7	6.0

motif. Also, β-Pu is $C2/m$, where the only difference between the two space groups $C2/m$ and Cm is an axis of twofold rotation perpendicular to the mirror plane. (Of course, in the real structures there is also a slight change of atomic positions.) The reduced space group of Cm for δ-Pu yields a viable path for the $\delta \leftrightarrow \alpha'$ phase transformation of Pu and Pu alloys. It has been shown that, at low pressures ($\sim$0.4 GPa), δ transforms first to β' then to α' in Pu-Ce [16] and Pu-Al [17] alloys. Given how close the space groups are between the reduced space group of Cm for δ-Pu and $C2/m$ β-Pu, this intermediate transformation to β makes sense.

A second important consequence of these calculations is that the structure is not centrosymmetric (defined as $x = -x$; $y = -y$; $z = -z$). Classical crystallography assumes spherical atoms occupy each lattice site and that fcc crystals are centrosymmetric. However, the above arguments show that this is a flawed idea for δ-Pu. The electronic structure (dominated by $5f$ states) produces bonding in the δ phase of pure Pu with largely varying strengths between the 12 nearest neighbors, thus making the crystal highly anisotropic and one that is the least applicable candidates for centrosymmetry compared to other fcc metals.

If one is to imagine a spectrum of isotropy, aluminum would reside on one side and plutonium on the other. With this in mind, we performed the same calculations on aluminum, which is well known to be the most isotropic fcc metal [18,19]. The results, which are in the same units as the Pu results, lie within 7.55–7.57 for the nearest-neighbor bond strengths. The slight variation in the resulting numbers is numerical noise. In other words, the method used above shows aluminum to have bond strengths for the 12 nearest neighbors which are identical, further supporting that Al is a highly isotropic metal.

The reduction of symmetry of δ-Pu illustrated above clarifies recent experimental results, such as those from Lawson *et al.* [20,21] that suggest a tetragonal distortion occurs in Ga-stabilized δ-Pu. In the work by Lawson *et al.* [20,21], neutron diffraction revealed that the widths of the peaks were temperature dependent for $\mathrm{Pu}_{0:98}\mathrm{Ga}_{0:02}$. As the sample was cooled, peak broadening occurred, increasing with subsequent cooling cycles. This effect disappeared when heated to 650 K. The diffraction peaks were anisotropic, which were modeled by assuming a small tetragonal distortion to the crystal. Because the changes of the diffraction peaks were observed at low temperatures, it is

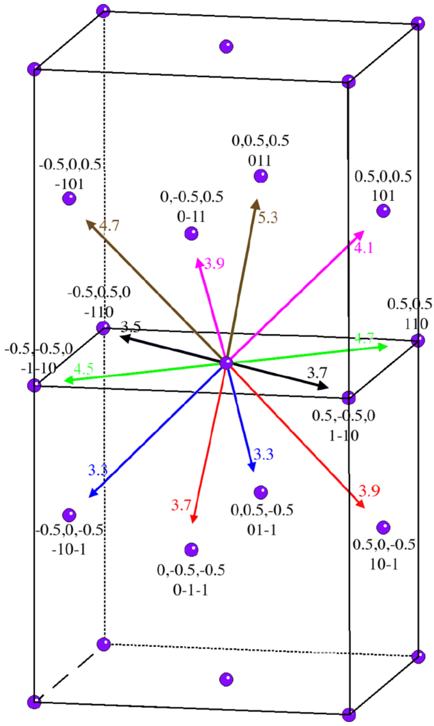

FIG. 3 (color online). Two stacked fcc unit cells with the central atom showing the 12 nearest neighbors. In the case of pure plutonium, the 12 bonds with the nearest neighbors vary widely with strength and can be separated into six pairs. When the fcc lattice is combined with the motif of these bond strengths, the resultant structure is monoclinic Cm.

possible that they are due to the anisotropic response of the δ-Pu matrix to the ingrowth of monoclinic α'-Pu particles that form during an isothermal martensitic phase transformation at low temperatures [22]. If one introduces precipitates or defects such as vacancies, interstitials, dislocations, and/or He bubbles [23] into an anisotropic medium, the variation in bond strength will cause the lattice to extend more in the soft directions and less in the rigid directions. Thus, tetragonal, orthorhombic, or monoclinic distortions in aged Ga-stabilized δ-Pu are logical, because precipitation of second-phase particles or the accumulation of damage will strain the lattice and contract or expand it disproportionately in different directions. Also of note is the small value of C$'$ for δ-Pu [9,24,25], which implies a soft response of the system to a volume-conserving tetragonal distortion.

Taking our approach one more step, we may now repeat the above calculations with a Ga atom in the central position of our 27-atom supercell and being subject to the displacement. In this case, we find that the energy response is more uniform than for pure Pu (see Table I). Most all of the bond strengths are near $F = 6$ with the exception of $[010]$ ($F = 7.0$), $[0\bar{1}1]$ ($F = 7.3$), and $[10\bar{1}]$ ($F = 4.4$). Why these bond forces are so high and low in value is not clear; however, the other 9 bonds are rather uniform. This uniformity in force implies that the bond strengths surrounding the Ga atom are higher in symmetry, thus supporting a higher-symmetry structure. In other words, these calculations illustrate why Ga acts to stabilize the high-symmetry fcc δ phase at room temperature by making the bond strength about the Ga atom less anisotropic.

The extended x-ray absorption fine-structure spectroscopy results of Cox *et al.* [26] support our calculations for both the pure Pu and the Pu-3.7 at. % Ga alloy. In their experiments on Ga-stabilized δ-Pu, it was observed that the local structure of plutonium about the Ga atoms was well defined and similar to a typical fcc metal. However, the local structure of plutonium around Pu atoms was disordered. Our calculations show exactly this: The bonds in pure Pu are highly anisotropic and thus produce a "poor" fcc structure, whereas the bonds about a Ga atom are less anisotropic and thus produce a more typical or "better" fcc structure, albeit not as good as aluminum.

In conclusion, we have shown that, when an fcc lattice is joined with the calculated anisotropic bonding of the 12 nearest neighbors as the motif (lattice + motif = space group), the resultant space group of pure δ phase Pu is Cm rather than $Fm\bar{3}m$. Our results enlighten why α-Pu is the only metal with a monoclinic ground state, reveal that δ-Pu does not have a center of symmetry, and lend a fundamental explanation for the tetragonal distortion purported to occur in Ga-stabilized δ-Pu as defects are introduced or as lattice damage is accumulated. Furthermore, our calculated bond strengths about a Ga atom in a 3.7 at. % Ga alloy show that the bonds are more uniform and symmetric, illuminating how Ga plays a stabilizing role for the δ phase at room temperature where the monoclinic α phase is observed in pure Pu. Finally, these results use first-principles theory in a novel way and systematically illustrate that an expansion of classical crystallography that accounts for anisotropic electronic structure can be used to explain complicated materials in a way previously not considered.

This work was performed under the auspices of U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

---

*Corresponding author.
Electronic address: moore78@llnl.gov

[1] F. D. Bloss, *Crystallography and Crystal Chemistry* (Holt, Rinehart and Winston, New York, 1971).
[2] R. C. Albers, Nature (London) **410**, 759 (2001).
[3] S. S. Hecker, Metall. Mater. Trans. A **35**, 2207 (2004).
[4] H. L. Skrivers, O. K. Andersen, and B. Johansson, Phys. Rev. Lett. **41**, 42 (1978).
[5] J. L. Smith and E. A. Kmetko, J. Less-Common Met. **90**, 83 (1983).
[6] S. Y. Savrasov, G. Kotliar, and E. Abrahams, Nature (London) **410**, 793 (2001).
[7] K. T. Moore *et al.*, Phys. Rev. Lett. **90**, 196404 (2003).
[8] G. van der Laan *et al.*, Phys. Rev. Lett. **93**, 097401 (2004).
[9] J. Wong *et al.*, Science **301**, 1078 (2003).
[10] H. M. Ledbetter and R. L. Moment, Acta Metall. **24**, 891 (1976).
[11] R. J. McQueeney *et al.*, Phys. Rev. Lett. **92**, 146401 (2004).
[12] R. Stedman and G. Nilsson, Phys. Rev. **145**, 492 (1966).
[13] D. E. Laughlin, M. A. Willard, and M. E. McHenry, in *Phase Transformations and Evolution in Materials*, edited by P. Turchi and A. Gonis (The Minerals, Metals and Materials Society, Warrendale, PA, 2000), p. 121.
[14] P. Söderlind and B. Sadigh, Phys. Rev. Lett. **92**, 185702 (2004).
[15] P. Söderlind *et al.*, Phys. Rev. B **66**, 205109 (2002); **70**, 144103 (2004).
[16] R. O. Elliot and K. A. Gschneidner, Jr., U.S. Patent No. 3,043,727 (1962).
[17] E. G. Zukas *et al.*, in *Proceedings of an International Conference on Solid → Solid Phase Transformations*, edited by H. I. Aaronson *et al.* (The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Littleton, CO, 1981).
[18] H. W. King, J. Mater. Sci. **1**, 79 (1966).
[19] B. Predel and W. Gust, Mater. Sci. Eng. **10**, 211 (1972).
[20] A. C. Lawson *et al.*, Philos. Mag. B **80**, 1869 (2000).
[21] A. C. Lawson *et al.*, Philos. Mag. B **85**, 2007 (2005).
[22] T. G. Zocco *et al.*, Acta Metall. **38**, 2275 (1990).
[23] A. J. Schwartz *et al.*, Philos. Mag. **85**, 479 (2005).
[24] X. Dai *et al.*, Science **300**, 953 (2003).
[25] G. Robert, A. Pasturel, and B. Siberchicot, J. Phys. Condens. Matter **15**, 8377 (2003).
[26] L. E. Cox *et al.*, Phys. Rev. B **51**, 751 (1995).