

Electronic and vibrational properties of Pu₃Ga: A theoretical explanation for the phonon softening observed in Pu-Ga alloys

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By using the density functional theory plus U (DFT+ U) method and taking spin-orbit coupling into account, we investigate the electronic and phonon properties of Pu₃Ga. Most interestingly, we find that there is a significant phonon softening in the transverse acoustic branch at the L point in the Brillouin zone. Via bond strength analysis, we reveal that the nearest-neighbor bond strengths in the face-centered-cubic lattice are weaker around Ga atoms, which is responsible for the observed phonon softening.

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I. INTRODUCTION

Plutonium (Pu) is familiar to people for its important role in nuclear energy and weapons. From a basic point of view, Pu is the most complex element in the periodic table. Due to the middle position in the actinide series (ranging from thorium to lawrencium), the $5f$ electrons show both localized and itinerant characters in Pu metal. Generally, the $5f$ states in light actinide metals before Pu are itinerant, while those in heavy actinide metals after Pu are localized [1]. The unique and complex electronic structure leads to many odd physical properties of Pu metal. For instance, with even a very little provocation, Pu can change its density by as much as 25% [2]; Pu can be as brittle as glass or as malleable as aluminum; Pu has six different kinds of solid allotropes, among which the δ phase shows a negative thermal expansion coefficient [2]; Pu is extremely dense (more than twice as dense as iron) [3]; and Pu is highly reactive in air and strongly reducing in solutions, forming multiple compounds and complexes in the environment or during chemical processing [1]. Among all allotropes, δ -Pu is the most wanted by engineers because it is of high ductility and thus easy to operate. However, pure δ -Pu is only stable from 593 K to 736 K and easily transforms to the monoclinic α phase at room temperature or below [4]. It has already been found that alloying with few amounts of IIIB elements, including aluminium (Al), gallium (Ga), indium (In), and thallium (Tl), can stabilize δ -Pu at room temperature and below [5]. Different from pure δ -Pu, the alloyed Pu in δ phase shows a positive thermal expansion coefficient. Until now a full understanding of the underlying physics for the stabilization of δ -Pu by alloying is still lacking.

Many theoretical studies have been carried out to study the δ stabilization by Al/Ga/In/Tl alloying. Earlier literatures claimed that the strong p - d - f hybridizations are responsible for the stabilization [6–9]. For example, an extended x-ray absorption fine structure study suggested that Al, Ga, and Sc impurities can diffuse the $5f$ bands to make them less

involved in bonding, leading to the stability of a d -bonded transition-metal-like phase [6]. Through analysis of electronic density of states, Hernandez *et al.* concluded that the Pu-Ga interactions are dominated by Pu $6d$ and Ga $4p$ hybridizations, as well as Ga $4s$ - $4p$ hybridizations [7]. Some other researchers focused on the α phase, believing that the key to the secret of those anomalies in the Pu phase diagram arguably hides behind the unusual geometry of the α -Pu structure [10,11]. Since Pu atoms at different sites in α structure have strong site-dependent correlation effects [12] and substituted Ga atoms at different sites also have various partial molar volumes [11], alloying with Ga will induce α -Pu alloys to be less stable. Conversely, δ -Pu-Ga alloys can be harder to decompose or transform.

Recently, Moore *et al.* suggested a new theory from a distinctive point of view [13]. By studying the varying bond strengths between a Pu atom and its 12 nearest Pu neighbors in both pure δ -Pu and 3.7 at.% Ga-alloyed δ -Pu, they have inferred that δ -Pu stabilization by Ga alloying is due to the reduced anisotropy. Although there are still controversies about their conclusions [14], this work proposes a way to study enigmas about Ga alloyed δ -Pu by comparing the situation of δ -Pu with different Pu_{1-x}Ga_x compounds. Along this line, several other researches also studied the general properties, including formation energies, phase diagrams, and electronic structures of Pu_{1-x}Ga_x as well as other Pu alloys in the δ phase [15–17].

Besides the stabilization by alloying, another well-known puzzle for δ -Pu is the discrepancy between theoretically calculated and experimentally measured phonon dispersion curves along the Γ - L direction [18–20]. In 2003, Dai *et al.* calculated the phonon dispersion curves for δ - and ϵ -Pu using the dynamical mean field theory (DMFT) [21]. They observed a considerable softening of the transverse acoustic phonons around the L point and claimed that the δ phase may be close to an instability with a doubling of the unit cell. Later, an inelastic x-ray scattering (IXS) experiment was carried out by Wong *et al.* [19]. The experiment qualitatively validates the main predictions of the previous DMFT calculation: a Kohn-like anomaly in one transverse acoustic branch along the [011] direction and a large softening of the two acoustic branches along the [111]

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direction. However, the phonon softening along the [111] direction observed in the experiment is much larger than the prediction in the previous DMFT calculation. Until now, the reason for this discrepancy remains undiscovered. Recently, Söderlind, *et al.* recalculated the phonon dispersion curves through standard density functional theory calculations, observing similar results as reported in Ref. [22]. They have proposed that the discrepancy at the L point may be due to the fact that the sample used for the IXS experiment was a δ -Pu-Ga alloy while all theoretical work has modeled unalloyed δ -Pu [22]. However, there are no further confirmations about this point.

Since the IXS experiment is carried out on δ -Pu-Ga samples and Pu_3Ga is a significant decomposition product when δ -Pu-Ga alloys slowly retain to the mixed α -Pu [23] which is more thermodynamically stable, we focus on Pu_3Ga as a reference to explore the influences of Ga on the vibrational properties of δ -Pu. Moreover, Pu_3Ga shares a similar fcc lattice structure with δ -Pu. Previous studies have revealed that the local spin density approximation (LSDA)+ U method can to some extent reproduce reasonable physical properties for the δ phase of Pu [24,25]. Hence, as a first step we adopt the LSDA+ U method in the present work. Our studies discover that due to different bonding strengths, there exists a larger phonon softening along the Γ -L direction in the Brillouin zone of Pu_3Ga . Thus it is suggested that the experimentally observed phonon softening comes from Ga atoms which can change the bonding strengths within δ -Pu.

II. METHODOLOGY

Our first-principles calculations are carried out by using the Vienna *ab initio* simulation package (VASP) [26]. The projected augmented wave method [27,28] is employed to describe the electron-core interactions. An energy cutoff of 500 eV is set for the plane wave basis. Following several previous theoretical studies, we adopt local spin density approximation (LSDA) [29,30] for the exchange-correlation potential. δ -Pu has the fcc lattice with 4 Pu atoms in each cubic cell. As with δ -Pu of the fcc lattice symmetry, in the unit cell of Pu_3Ga there are three Pu atoms occupying face center positions and a nonmagnetic Ga atom at the corner. For the collinear magnetic orders, the three magnetic Pu atoms would lead to magnetic frustration [31]. Therefore, magnetic moments on all Pu atoms are kept in the same direction. But we have also constructed a simple antiferromagnetic state following Söderlind and Landa [32] to compare the energies between ferromagnetic and antiferromagnetic states. Meanwhile, the spin-orbit coupling (SOC) effect is included all through the calculations and the easy axis is defaulted along the [001] direction. The Pu $5f$, $6s$, $6p$, $7s$ and the Ga $3d$, $4s$, $4p$ electrons are included as valence electrons. For the correlated $5f$ orbitals, the on-site Coulomb repulsion is set to 4.5 eV and the exchange parameter J is set to 0.51 eV, the same value as in Ref. [12]. We fix the lattice constant at a series of values and relax the internal positions of the atoms until the residual forces on all relaxed atoms were smaller than $0.005 \text{ eV}/\text{\AA}$, thus the lattice parameter is tested by hand. For the computations of phonon band structures, we have used the density functional perturbation theory (DFPT) with the help of PHONOPY package [33]. The reciprocal space of

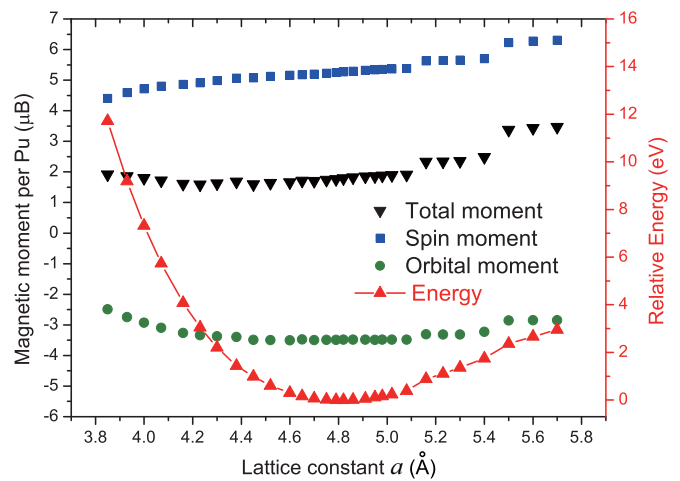


FIG. 1. The total energy and magnetic moments against the lattice constant of Pu_3Ga . The energies marked on the right vertical axis are relative to the energy of Pu_3Ga with $a = 4.82 \text{ \AA}$. The magnetic moments include the spin moment and orbital moment, both of which are averaged on every Pu atom. The orbital moment is opposite to the spin moment in sign, thus the total moment is partially canceled.

the 4-atom Pu_3Ga unit cell was sampled with a MonkhorstPack $9 \times 9 \times 9 \mathbf{k}$ mesh. For phonon and bond strength calculations, the unit cell is enlarged to $2 \times 2 \times 2$ and the \mathbf{k} mesh is $4 \times 4 \times 4$.

III. RESULTS AND DISCUSSIONS

We have calculated the total energy against lattice constant of Pu_3Ga , which is shown in Fig. 1. Using Murnaghan equation of state, the fitted equivalent lattice parameter is $a = 4.804 \text{ \AA}$, in reasonable agreement with the experimental value of 4.507 \AA [34]. It should be noted that spin-orbital couplings are included in all our calculations. Our calculations result in a magnetic ground state for Pu_3Ga with a nonzero magnetic moment on each Pu atom as shown in Fig. 1. The spin moment and orbital moment are in opposite directions, therefore the total magnetic moment is much smaller than the spin moment, in accordance with a previous classic work [35]. The calculated magnetic property of Pu_3Ga is consistent with the conclusions made by Havela *et al.* By using an around mean field method together with the LDA+ U calculations, they have studied the $5f$ occupancies in a series of Pu compounds as well as δ -Pu [36]. They find that the $5f$ occupancy plays a key role in determining the magnetism of the material. PuC and PuSb compounds with the $5f$ occupancies smaller than 5.2 are magnetic, while δ -Pu, Pu_2C_3 , and PuSe *etc.* with larger $5f$ occupancies are nonmagnetic. Our calculations yield that the $5f$ occupancy for Pu atoms in Pu_3Ga is around 5.1, lying within the magnetic range defined by Havela *et al.* Thus Pu_3Ga is supposed to be magnetic in its ground state. This result also accords with the magnetization experiment finding that Pu_3Ga is antiferromagnetic (AFM) under 40.3 K [37]. Nevertheless, the exact magnetic configuration is still unknown. In our calculations, the ferromagnetic (FM) state for Pu_3Ga is more stable than the tested collinear AFM state by 0.049 eV for an 8-atom magnetic unit cell. There probably exist noncollinear

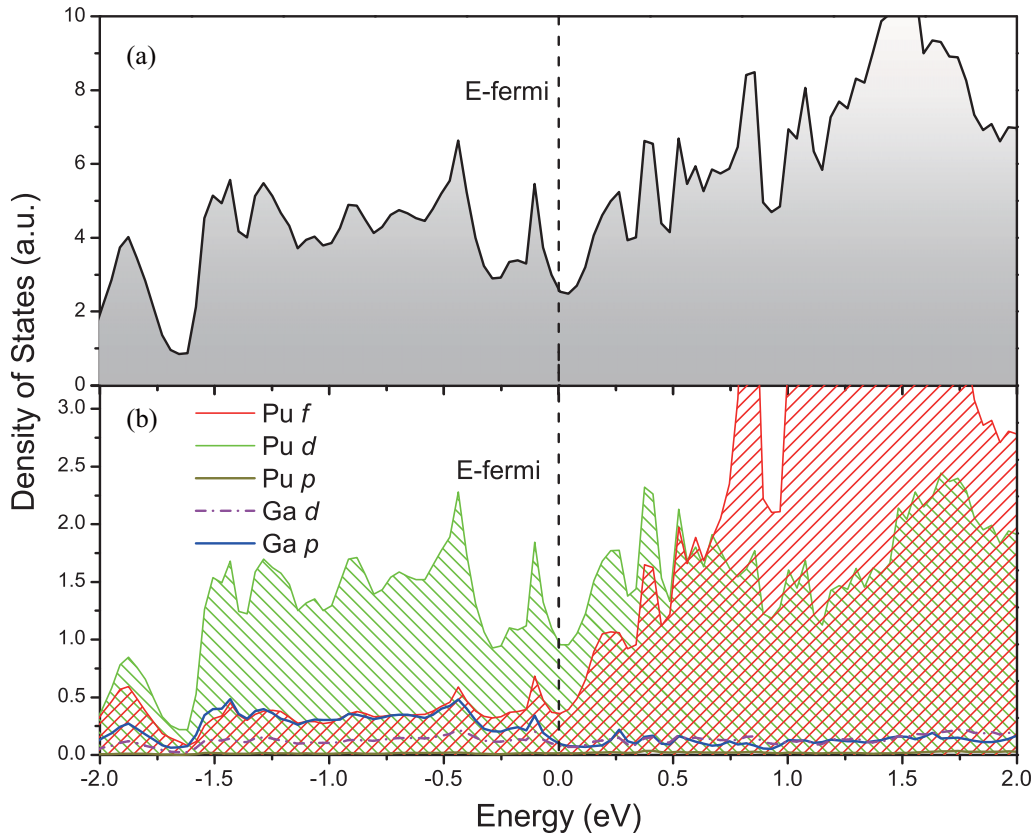


FIG. 2. (a) Total electronic density of states and (b) partial electronic density of states projected on Pu and Ga orbitals in Pu_3Ga . The Fermi energy is set to zero.

AFM states which can be more stable than the FM state. The single-particle approximation used in DFT is also limited. More accurate theoretical methods are encouraged to be used and more complex AFM configurations should be tried to explore the ground-state properties of Pu_3Ga , however, they are beyond the scope of the current paper.

The total electronic density of states (DOS) and partial density of states (PDOS) projected on Pu f , d , p orbitals and Ga d , p orbitals are depicted in Fig. 2. One can see that there are strong hybridizations between the $5f$ and $6d$ states of Pu at the two sides of the Fermi energy. Besides, we also notice a wide hybridization area for the Pu $5f$, $6d$ states and the Ga $3d$, $4p$ states from the Fermi energy to 2.0 eV below the Fermi level. These results indicate that the existence of Ga atoms strongly influences the electronic states of δ -Pu. The hybridization between Pu and Ga states is in agreement with what was reported in Ref. [7], where it was even proposed that the Pu $6d$ and Ga $4p$ electronic hybridizations stabilize the fcc structure for Ga-doped δ -Pu. No matter how the existence of Ga atoms stabilizes the δ phase, it is true that Ga substitution will largely change the electronic structures of Pu. As we will discuss as follows, the change in electronic structures finally leads to the change of the vibrational properties of the δ -Pu.

In comparison with the vast studies on the stabilization mechanism and magnetic property of δ -Pu, fewer efforts are dedicated to comprehending the phonon softening behavior at the L point. On the other side, various physical properties such as sound velocities, elastic constants, and heat capacity,

can be derived from the phonon dispersion curves (PDCs) of a material. Therefore, a full theoretical understanding on the PDC of δ -Pu is also needed. Firstly, we recalculate the PDC for pure δ -Pu using the LSDA+ U method. We show our result in Fig. 3(a) together with the previous experimental data [18–20]. Our obtained PDCs are very similar to the DMFT result reported in Ref. [21]. This fact is probably because that correlation effect of $5f$ electrons in δ -Pu, which DFT+ U fails to capture precisely, is not large enough to strongly influence the bonding strengths. Compared with the experimental result in Ref. [19], the most obvious difference lies on the transverse acoustic (TA) branch along the [111] direction. Our calculations cannot reproduce the phonon softening observed in experiment. We notice that although the DMFT calculations can give a down-bending at the L point [21], the frequency of the TA branch at the L point is nearly twice that of the experimental value. Since the DMFT results for other phonon branches accord very well with the experiment, we would like to consider that there are still unknown mechanisms beneath the discrepancy at L . Recently, Söderlind recalculated the PDCs for δ -Pu by using two different kinds of methods. The full-potential linear muffin-tin orbital method combined with compressive sensing lattice dynamics can yield a mildly bent TA branch at the L point, yet the positive kink along the [011] direction is missing [22]. In contrast, the exact muffin-tin orbital method with compressive sensing lattice dynamics is in good agreement with the experimental data along the [111] direction around

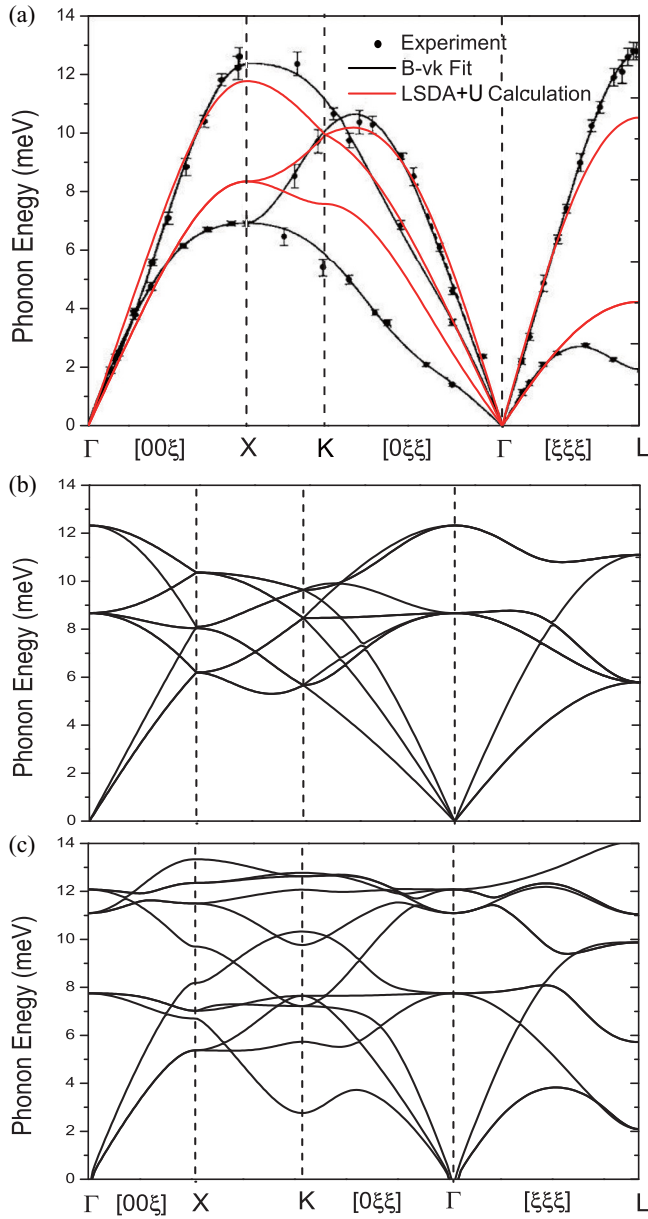


FIG. 3. (a) Phonon dispersion curves for pure δ -Pu calculated with LSDA+ U method including SOC in this work (red line) compared with those from inelastic x-ray scattering experiment for δ -Pu-2 atomic % Ga alloy at room temperature. The solid curves are the fitted lines to the experimental data with a fourth-nearest-neighbor Born-von Kármán model [19]. (b) and (c) are calculated phonon dispersion curves for pure δ -Pu of a 4-atom unit cell and Pu_3Ga , respectively.

the L point, while along the $[001]$ direction the deviation is irremediable [22]. Therefore, the phonon softening at the L point remains a puzzle for δ -Pu. We will show next that this puzzle can be solved to a certain degree by comparing the PDCs of Pu_3Ga with that of δ -Pu.

In order to clearly differentiate the PDCs of Pu_3Ga with that of δ -Pu, we recalculate the PDCs of δ -Pu in the reciprocal space of a four-atom supercell. The calculated PDCs for the four-atom δ -Pu cell as well as those for Pu_3Ga are shown in Figs. 3(b) and 3(c), respectively. Since the atomic structure

of Pu_3Ga is obtained by substituting a Pu atom with a Ga atom, the degeneracies of the optical modes of Pu_3Ga and δ -Pu are reasonably different. The degeneracy of the higher optical modes is lifted in Pu_3Ga and the frequencies are also larger than those in δ -Pu. Next, we focus on the lowest transverse acoustic branches. Obviously, the two transverse branches along the $[001]$ direction are nearly degenerate both in Pu and in Pu_3Ga , whereas, at the L point along the $[111]$ direction, as shown in Fig. 3(c), there is a huge softening of the transverse mode in PDCs of Pu_3Ga , which is distinguished from PDCs for pure Pu as in Fig. 3(b). Because of this notable anomaly at L discovered in Pu_3Ga , it is predictable that the mixture of δ -Pu and Pu_3Ga also has a considerably large softening at the L point in the transverse acoustic modes. As Ref. [22] pointed out, the δ -Pu samples prepared for experiments are not pure Pu metals; instead, they are Pu-Ga alloys with at least 0.1 at.% Ga, which possibly contain Pu_3Ga component. Therefore, our calculated phonon softening at the L point in Pu_3Ga can just account for the experimentally observed prominent anomaly at the L point in Pu-Ga alloys and confirm the conjecture of Ref. [22]. In addition to the difference at the L point, along the $[011]$ direction there are other pronounced characters in PDCs for Pu_3Ga . The transverse branch has a softening at the K point and a Kohn-like anomaly along the $[011]$ direction. This Kohn-like anomaly near K along the $[011]$ direction might correspond to the small Kohn-like anomaly found in experiments of δ -Pu alloyed with small part of Ga [18–20]. Besides, the frequencies of the acoustic modes of Pu_3Ga at the X point and K point along $[011]$ are much lower than those of δ -Pu.

To understand the difference in phonon dispersions at the L point of δ -Pu and Pu_3Ga , we then investigate the bond strengths in them. The method proposed by Moore *et al.* [13] has been employed. In order to eliminate the effect of periodic images, the 4-atom cell is enlarged by $2 \times 2 \times 2$. Then an atom selected as the central atom is displaced along each of its 12 nearest-neighbor directions by about 2% of the original distance. The total energies of the 32-atom cell before and after the displacement of the central atom have been calculated and the changes of the energies which represent the bond strengths are marked as shown in Fig. 4. From the symmetry point of view, in δ -Pu the displacements in the 12 directions must produce the same energy response [14]. Since we have performed spin-polarized calculation with SOC effect, the magnetic moments have destroyed the cubic symmetry of the system. Now that δ -Pu is of tetragonal symmetry with all the magnetic moments of Pu pointing to the $[001]$ direction, the 12 nearest bond strengths can be different. As demonstrated in Fig. 4(a), the largest energy change, i.e., the representative of bond strength, is 10.72 meV and the smallest energy change is 9.63 meV. The difference in the energy responses when central Pu moves in different directions is due to the SOC effect, the slight change of the magnetic structure and even the finite accuracy of the numerical calculations, but the average bond strength can still have a reference value when considering the bond strengths in Pu_3Ga .

On the contrary, in Pu_3Ga the bond anisotropy is enhanced since the symmetry is lowered. As shown in Fig. 4(b), the central Ga atom is in the same chemical environment with a Pu atom in pure δ -Pu, and thus the bond strengths are comparable. Obviously, the bond strengths of Ga and its

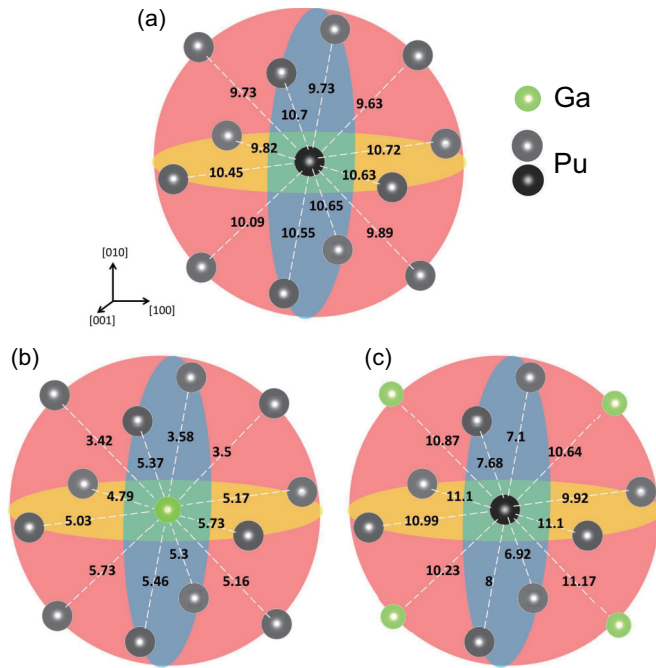


FIG. 4. Schematic plots of a central atom and its 12 nearest neighbors in (a) δ -Pu and (b), (c) Pu_3Ga , where (b) demonstrates a central Ga atom and 12 nearest Pu atoms and (c) shows a Pu atom and 12 nearest neighbors including both Pu and Ga atoms. The white dashed lines denote the bonds between central atoms and the nearest neighbors and the numbers marked on the bonds represent the response energy after displacing the central atom along the corresponding direction by 2%, in units of meV. The red, blue, and yellow planes are only guides to the eyes to illuminate the planes at which different neighboring atoms locate.

neighboring Pu atoms are much smaller than those in pure Pu. The results indicate a softening of the displacements of Ga atoms. For the bonds between a Pu atom and its nearest neighbors in Pu_3Ga , the average strength does not deviate much from that in δ -Pu. However, the bond strengths along all 12 directions change much more remarkably. Actually, it is shown in Fig. 4(c) that the largest energy difference can be as high as 4.0 meV, nearly four times that in pure Pu. In

summary, the Ga substitution for Pu in δ -Pu can lead to easier atomic displacements and larger bond anisotropy.

IV. CONCLUSION

To summarize, we have systematically studied the electronic and vibrational properties for Pu_3Ga , the stable compound product during the decomposition process of Pu-Ga alloys. Our LSDA+ U calculations predict that Pu_3Ga is magnetic in the ground state, in agreement with the experiment. The phonon dispersion curves are then calculated for both Pu_3Ga and δ -Pu. We find that there is a significant softening for the transverse acoustic phonon of Pu_3Ga at the L point of the Brillouin zone. Although the adopted LSDA+ U method has its limitations, our results provide a possible explanation for the experimentally observed phonon softening in δ -Pu-Ga alloy samples, considering that previous theoretical studies have neglected the influences of Ga atoms and missed the softening behavior. Moreover, the bond strengths of a central atom and its 12 nearest neighbors are calculated for both δ -Pu and Pu_3Ga , showing that the bond anisotropy of Pu_3Ga is greater than that of pure Pu, while the bond strengths of Ga and its nearest neighbors in Pu_3Ga are much smaller than those in pure δ -Pu. Therefore, the weakening of the bond strengths is probably responsible for the phonon softening behavior. Our work can be an inspiration for studies with more accurate methods, such as the DFT+DMFT method, to further explore the puzzles of δ -Pu in the future.

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