The abnormal lattice contraction of plutonium hydrides studied by first-principles calculations*

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Pu can be loaded with H forming complicated continuous solid solutions and compounds, and causing remarkable electronic and structural changes. Full potential linearized augmented plane wave methods combined with Hubbard parameter U and the spin–orbit effects are employed to investigate the electronic and structural properties of stoichiometric and non-stoichiometric face-centered cubic Pu hydrides (PuH_x, $x = 2$, 2.25, 2.5, 2.75, 3). The decreasing trend with increasing x of the calculated lattice parameters is in reasonable agreement with the experimental findings. A comparative analysis of the electronic-structure results for a series of PuH_x compositions reveals that the lattice contraction results from the associated effects of the enhanced chemical bonding and the size effects involving the interstitial atoms. We find that the size effects are the driving force for the abnormal lattice contraction.

Keywords: plutonium, density functional theory, strongly correlated electron system, crystal structure

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1. Introduction

Understanding the 5f states of actinides has always been the key of this engaging and challenging field.[1–9] Among this series, Pu lies just at the critical point where the delocalization to localization transition of the 5f electrons in the actinides occurs, which results in the occurrence of numerous bizarre properties. Increasing effort has been taken to deeply understand the nature of the 5f electrons in Pu materials, which has been comprehensively reviewed by Moore and van der Laan.[10] However, there are still many unanswered questions and persisting arguments on the topics of electronic structure, magnetism, and bonding character. Furthermore, due to the mysterious aging of Pu and the lack of enough experimental observations, its complex properties become even more puzzling. Therefore, more and more first-principles techniques, from the traditional density functional theory (DFT) to exact strongly-correlated electronic structure calculation methods such as dynamical mean field theory (DMFT), have been used to explore the electronic structures of Pu materials during the last three decades.[11] Recently, with the development of *in-situ* surface analysis techniques and high performance computation, more and more experimental and theoretical attention has been particularly paid to investigations of the Pu–H surface reaction and to probe into the localization/delocalization transition of the 5f electrons and the chemical bonding of H atoms on the Pu surface.[12–16] Unfortunately, almost no literature is available on the electronic structure calculations of Pu hydrides, which can be as important as the widely studied Pu oxides in the fields of surface chemistry.[17–19]

The basic features of the Pu–H system have been reported for more than fifty years.[20] However, the quick or even catalyzed reaction and the pulverization and pyrophoricity of the hydrides make *in-situ* characterizations extremely difficult. The classic works of Haschke *et al*., Ward *et al*., and Bartscher *et al*.[21–23] established the basic thermodynamics and kinetics of the Pu–H reaction, a rough phase diagram, and the bonding character. The results showed that Pu reacts with H forming a cubic dihydride over the range of x (H to Pu atomic ratio) from 1.9 to 2.7. Stoichiometric PuH_2 has a face-centred cubic (fcc) CaF_2-type structure in which the tetrahedral interstices are occupied by H atoms (denoted as H_t). For $x > 2.0$, continuous solid solution PuH_x exists over the range of $2.0 < x < 3.0$ when extra H atoms enter into the octahedral interstices (denoted as H_o). However, when $x > 2.7$, the cubic dihydride undergoes a partial phase transition followed by the formation of a hexagonal close packed (hcp) LaF_3-type structure; thus, fcc and hcp PuH_3 phases coexist in this H range. Interestingly, the experimental investigation by Muromuro *et al*.[24] showed that the cubic parameters decrease regularly with increasing x in the range of $2.0 < x < 2.7$, which appears to violate the conventional conception. However, no further knowledge is available to elucidate the abnormal behavior. In the present paper, we theoretically explore the lattice parameter–composition relationship of Pu hydrides by using the full potential linearized augmented plane-wave (FPLAPW) basis within the DFT+U framework and considering the strong Coulomb correlation

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between the localized Pu 5f electrons.[25]

2. Method of calculations

In this paper, we theoretically explore the lattice parameter–composition relationship of Pu hydrides (PuH_x, $x = 2$, 2.25, 2.5, 2.75, 3) by using FPLAPW methods implemented in the WIEN2K package.[26] The calculation models of non-stoichiometric Pu hydrides are constituted by symmetrically removing H_o atoms from PuH_3, as shown in Fig. 1. All the calculations are performed on the conventional cells of PuH_x, each containing four formula units constituting Pu_4H_{4x}. The generalized gradient approximation (GGA) is chosen as the exchange–correlation potential. The electronic configurations of the valence electrons are Pu-$5f^6 7s^2$ and H-$1s^1$, respectively. For Pu, its $6s^2 6p^6$ semicore states are treated as local orbitals. The muffin-tin radii R_{mt} of Pu and H are chosen as 1.22 Å and 0.48 Å, respectively. The charge density is Fourier expanded up to $G_{max} = 20$ Ry, and the cut-off parameter $R_{mt}K_{max}$ is set to be 4. The self-consistency is achieved demanding the convergence of the total energy to be smaller than 0.0001 Ry. Electronic structure calculations start with the optimization of K points, U, volume, and lattice parameters on the stoichiometric PuH_2 and PuH_3. The number of K points and the effective Hubbard parameter U_{eff} of Pu are optimized to be 2000 and 4.00 eV, respectively. Magnetic calculations show that the ferromagnetic (FM) phases of PuH_2 and PuH_3 are energetically more favorable than antiferromagnetic (AFM) and nonferromagnetic (NM) phases, which is in agreement with the available scatter experimental data.[27] Therefore, only the results of FM calculations are presented. All the calculation parameters for non-stoichiometric Pu hydrides are the same as those for PuH_2 and PuH_3. The spin–orbit (SO) coupling is included via a second variational step using the scalar relativistic eigenstates as the basis, in which all eigenstates with energies below 4 Ry are included. Furthermore, relativistic $p_{1/2}$ orbitals have been included to account for the finite character of the $p_{1/2}$ wave function at the nucleus. For comparison, pure GGA and GGA+U calculations without the SO coupling are performed as well. Due to the importance of relativistic effects of actinides,[28–30] the discussion is concentrated on the GGA+U+SO calculations.

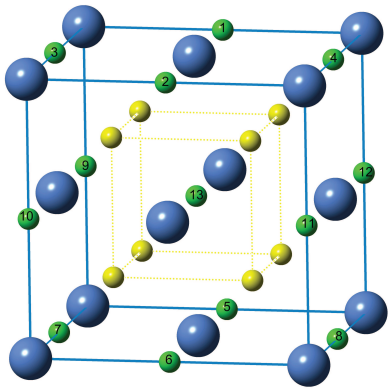


Fig. 1. (color online) Calculation model of the crystal structures of fcc Pu hydrides. The large and small balls denote Pu and H atoms, respectively. Eight H_t atoms locate on the dash-line frame. Three non-stoichiometric Pu hydrides are constituted as follows: $PuH_{2.75}$ by removing No. 9, 10, 11, and 12 H_o atoms; $PuH_{2.5}$ by removing No. 1, 2, 5, 6, 9, 10, 11, and 12 H_o atoms; $PuH_{2.25}$ by keeping only No. 13 H_o atom.

3. Results and discussion

In order to understand the stability of Pu hydrides with increasing x, the average binding energy per H atom $E_b(H)$ and the cohesive energy of PuH_x $E_{coh}(PuH_x)$ are defined as

$$E_b(H) = \frac{1}{x}[E(PuH_x) - E(Pu_{fcc})] - E(H_{atom}), \quad (1)$$

$$E_{coh}(PuH_x) = E(PuH_x) - E(Pu_{fcc}) - xE(H_{atom}). \quad (2)$$

The $E(Pu_{fcc})$ is calculated with the same methods as those used for Pu hydrides. The bulk modulus B is obtained from the Birch–Murnaghan equation-of-state (EOS) fit of the energy–volume relationship. In addition, the average ionic charge per Pu or H (H_t and H_o) atom is obtained by the topological analysis of the electron densities using the CRITIC program.[31] The calculated a, B, $E_b(H)$, $E_{coh}(PuH_x)$ and ionic charge are shown in Fig. 2. For comparison, the experimental lattice parameters of fcc Pu hydrides are redrawn in Fig. 2(a).[22] Although the theoretical values are overestimated owing to the intrinsic deficiency of the GGA, a basic agreement with the experimental observations is found in the lattice parameters of PuH_x. Other researchers found vacancies on the tetrahedral sites in PuH_x ($x > 2$) by neutron diffraction measurements.[23] For example, $PuH_{2.25}$ has 4%–5% tetrahedral vacancies, and $PuH_{2.65}$ has approximately 10% tetrahedral vacancies. So the calculation models in the current study basically agree with the experimental structure, and the hydrogen–vacancy interactions should be considered for the precise predication of the lattice parameters. The most remarkable feature is that the calculated lattice parameters of Pu hydrides contract with the increasing x. In a rule owing to the size effects, adding impurity atoms to stoichiometric actinide compounds forming hyperstoichiometric compounds increases the lattice parameters. However, some Pu compounds make an exception. For instance, measurements revealed that the accommodation of extra O atoms in the fluorite structure PuO_2 constituting $PuO_{2.25}$ leads to a vanishingly small increase in the lattice parameter.[32] Calculations based on the self interaction correction (SIC) indicated that the lattice parameter of $PuO_{2.25}$ is slightly smaller than that of PuO_2.[33] The lattice contraction reflects the localization/delocalization transition of the Pu 5f electrons in its oxides. The Pu 5f electrons become more delocalized as extra O atoms are added to PuO_2, then the bonding strength between Pu and O atoms correspondingly enhances, which results in the abnormal change of the lattice parameter. The same phe-

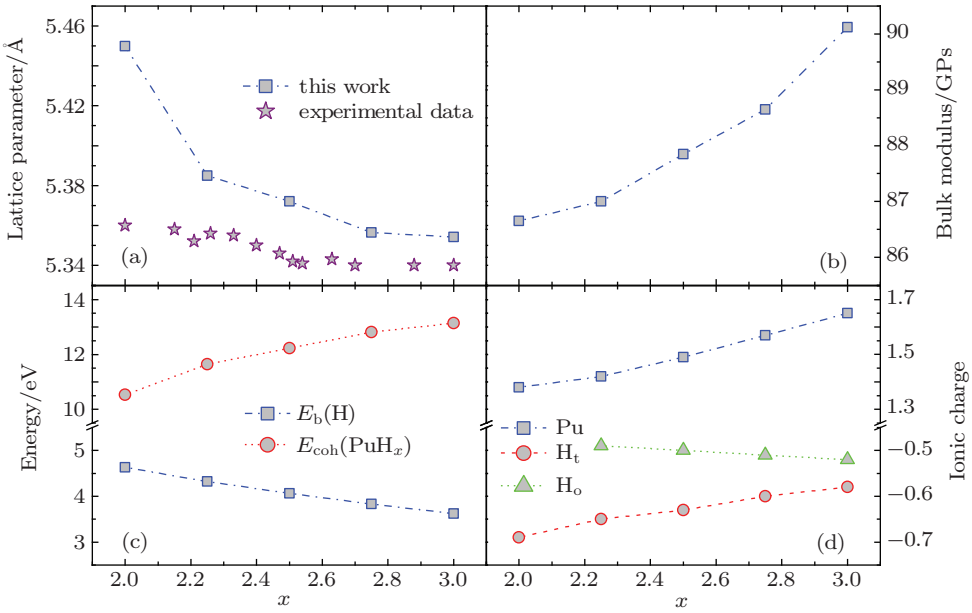


Fig. 2. (color online) Calculated (a) lattice parameter, (b) bulk modulus, (c) average binding energy per H atom, cohesive energy of PuH$_x$, and (d) average ionic charge per Pu or H (H$_t$ and H$_o$) atom. Note that the calculated E_b(H) and E_{coh}(PuH$_x$) are negative, therefore we take their absolute values.

nomenon appears in the analogues of Pu hydrides, i.e., the Ln hydrides.[34] Similar to Pu oxides, the addition of H atoms into PuH_2 has a profound effect on the electronic structure, however, the driving forces for the abnormal changes of the lattice parameters of the two Pu binary systems are different as addressed later. In addition, the absolute value of E_b(H) decreases whereas the absolute values of E_{coh}(PuH$_x$) and B increase with increasing x, which suggests that the binding strength of H to the lattice decreases whereas the overall binding strength of the lattice increases. The results can be elucidated by analyzing the calculated electronic structure and the chemical bonding. For the bulk modulus, under the condition of lacking experimental data, we find that the values of stoichiometric Pu hydrides in the GGA+U+SO framework are comparable to the experimental values of its ideal analogues, Ln hydrides.[35]

The total densities of states (TDOS) of some representative Pu hydrides in GGA+U+SO computations are displayed in Fig. 3, and the projected DOS (PDOS) of Pu 5f and 6d, H$_t$ and H$_o$ 1s are also shown. In order to analyze the Pu–H interaction, the expanded PDOS of Pu 6d, H$_t$ and H$_o$ 1s are presented. We find that all the Pu hydrides show some common grounds. Firstly, the valence (VB) and the conduction (CB) bands around the Fermi level E_F are dominated by Pu 5f electrons, whereas the contributions from H 1s and other orbitals of the Pu atoms are rather small. On-site Coulomb interaction U makes the localization of the 5f electrons strengthen, and the SO coupling makes the main peaks of the 5f VB states be well split. Secondly, all the Pu hydrides behave similarly in chemical bonding with the main hybridization interactions between Pu 6d and H 1s orbitals as shown by similarities in the position and shape of the peaks in their respective PDOS. Thirdly, all the Pu hydrides show a relatively weak metallic feature with a small amount of electrons traversing E_F in the GGA+U+SO framework. For PuH_3, the electrons traversing E_F are almost inappreciable, implying the potential insulating feature of PuH_3. Interestingly, very limited electric measurements showed the metal–insulator transition (MIT) of $PuH_2 \longrightarrow PuH_3$.[36] Further experiments, especially after Huiberts group's benchmark works on Y and La hydrides as switchable mirrors, have shown that the MIT is a rather robust one, occurring in all Ln metals close to the trihydride composition irrespective of the crystal structure.[37] Many theoretical attempts have then been devoted to predict the trihydride energy band especially the band gap but met with great difficulties.[38,39] In our previous work, we provided a theoretical evidence that the spectacular MIT occurs on the phase transformation from fcc PuH_2 to hcp PuH_3 by using the FPLAPW calculations without considering the SO coupling interactions.[35] In the present work, we are sure that the MIT of fcc $PuH_2 \longrightarrow$fcc PuH_3 is partially reproduced.

With the increase of x, some appreciable changes occur on the DOS. Firstly, the TDOS of PuH$_x$ downshifts to the low-energy side, implying the chemical bonding between Pu and the extra H atoms. Secondly, the peak width of the Pu 5f states becomes slightly broader, which is associated with the weak delocalized behavior of 5f and the weak 5f–6d–1s hybridization. A very small energy difference between Pu 5f and 6d orbitals can make partial 5f electrons fluctuate between 5f and 6d orbitals.[10] In the VB region, Pu 5f and 6d states are not fully separated in energy. Generally speaking, 5f electrons in metallic Pu are well localized and do not contribute to the

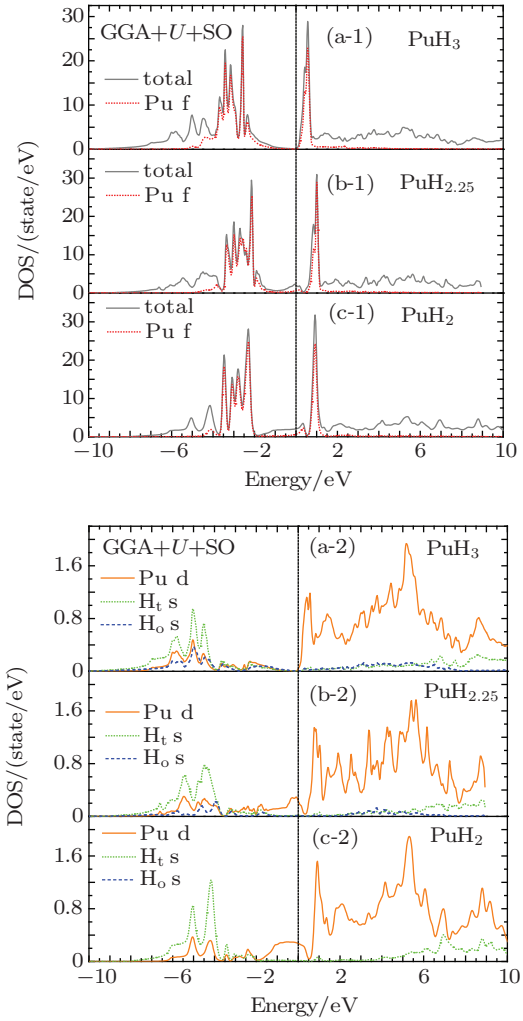


Fig. 3. (color online) Calculated total DOS and projected DOS for some representative Pu hydrides ((a) PuH_3, (b) $PuH_{2.25}$, (c) PuH_2). The E_F is scaled to zero and marked by the vertical dotted line.

chemical bonding in the solid phase. Thus, the Pu valence behavior is dominated by the 6d electrons, resulting in the significant hybridization with the ligand valence electrons and covalency. However, the Pu 5f electrons may exhibit more or less delocalized character depending on the chemical surroundings, which was supported by many theoretical and experimental findings on Pu compounds especially on Pu oxides. Although the hybridization interactions between Pu 6d and H 1s states become the main chemical bonding in Pu hydrides, we are sure that some weak covalent bonds arising from Pu 5f hybridization with Pu 6d and H 1s still exist. In addition, from the PDOS we also find that the hybridization mainly exists between Pu and H_t atoms, whereas the hybridization between Pu and H_o atoms is relatively weak. To some degree, the Pu–H bonds in Pu hydrides characterize a mixture of ionic and covalent components, just as the inherent bonding nature in most metal hydrides.[40] The interpretation on the chemical bonding is further substantiated by the analysis of the valence-electron-charge density and the difference electron-charge density shown in Fig. 4. The charge densities around Pu and H atoms both have a near spherical distribution slightly deformed toward the directions to their nearest-neighboring atoms, and there are clear covalent bridges between Pu and H_t. The difference electron-charge density contour map clearly indicates that charge transfers from Pu atoms to H atoms, mainly to H_t atoms. The relatively weak covalent bonds between Pu and H_o indicate that the total ionicity degree of PuH_x increases with the increase of x as shown in Fig. 2(d). The increasing ionicity degree of PuH_x results in the enhanced cohesion and partially accounts for the increase of bulk modulus and the decrease of lattice parameter.

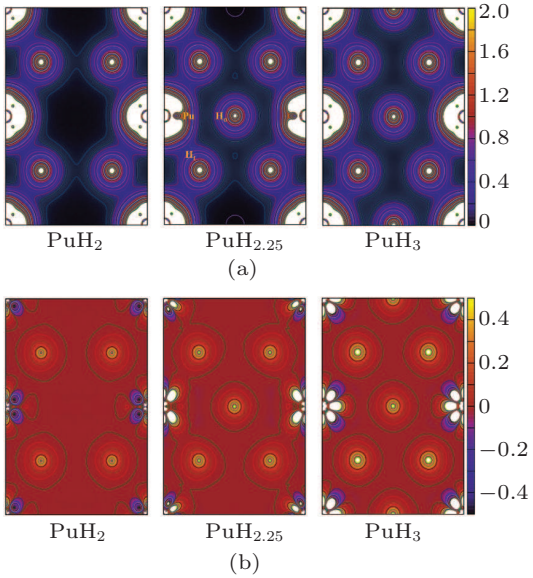


Fig. 4. (color online) Calculated (a) valence-electron-charge and (b) difference electron-charge density contour plots in the GGA+U+SO computation. The illustrations refer to the (1 1 0) plane, and the unit of electron charge density is $e/Å^3$.

The present findings basically reflect the mixed ionic–covalent bonding nature, and the Pu 5f electrons become slightly delocalized with the increase of x. Although the chemical bonding interactions between Pu and extra H_o adding to PuH_2 are relatively weak, the total chemical bonding interactions still enhance. However, the enhanced chemical bonding interactions in the hyperstoichiometric Pu compounds are not the definitive reason for the lattice contraction. The size effect can play an important role in the lattice contraction. Taking PuO_x for example, the combined effects of the enhanced chemical bonding interactions and the volume gain from the extra O atoms make the lattice parameter of $PuO_{2.25}$ almost unchanged with respect to that of PuO_2.[33] For the hyperstoichiometric Pu hydrides, the size effect must prevail over the hyperstoichiometric Pu oxides mainly due to the large size difference between H and O since the similar electronic structure changes happen on the two Pu compounds. In the fcc lattice, the radius of the octahedral interstice is 84% greater than that of the tetrahedral interstice, therefore the lattice strains induced by H_t atoms are remarkable and an appropriate expansion can minimize the lattice strains, thus an optimal atomic

bonding distance occurs between Pu and H_t atoms. In contrast, the much larger atomic distance between Pu and H_o atoms results in the tendency of decreasing atomic distance thus favoring the chemical bonding. The fact that H_t atoms leads to lattice expansion whereas H_o leads to lattice contraction is consistent with other theoretical findings on rare-earth hydrides.[34] A hypothetical crystal structure of fcc monohydride PuH_o in which all the octahedral interstitial sites are occupied by H atoms is constructed for the purpose of supporting the explanation. The calculated lattice parameter of PuH_o greatly decreases to be 5.1023 Å while that of $Pu(H_t)_2$ is $a = 5.4498$ Å, which powerfully accounts for the different size effects of H_o and H_t on the lattice contraction.

4. Conclusion

In summary, we have applied the FPLAPW approaches to investigate the electronic and structural properties of fcc Pu hydrides. The most attractive outcome is the successful prediction of experimentally observed lattice contraction with the increase of H composition. Our analysis on the electronic structure of Pu hydrides reveals that Pu hydrides have both covalent and ionic bondings, and the hybridization interactions between Pu 6d and H 1s are the dominant origin of the chemical bonding. However, the roles of H_t and H_o are remarkably different in the chemical bonding. Furthermore, a small amount of Pu 5f electrons undergo the localization–delocalization transition with the increase of x and participate in the chemical bonding, which suggests that the extra H atoms can more or less absorb Pu 5f electrons giving rise to the increase of ionicity of Pu hydrides. The overall enhanced chemical bonding and the different roles of H_t and H_o atoms in the chemical bonding may be the two important aspects in the explanation of lattice contraction and the decrease of the H binding energy of Pu hydrides, however, they are not the decisive reason. From the analysis of the interstitial size effect of H_t and H_o atoms and the comparison with the findings on nonstoichiometric PuO_x, we find that the interstitial size effect can be reckoned as the driving force for the lattice contraction. The small H atomic radius and the large atomic distance between Pu and H_o atoms result in the strong tendency of decreasing atomic distance thus favoring the chemical bonding.

References

[1] Chen J, Meng D Q, Du J G, Jiang G, Gao T and Zhu Z H 2010 *Acta Phys. Sin.* **59** 1658 (in Chinese)

[2] Wolfer W G 2000 *Los Almos Sci.* **26** 274

[3] Ao B Y, Wang X L, Chen P H, Shi P, Hu W Y and Yang J Y 2010 *Acta Phys. Sin.* **59** 4818 (in Chinese)

[4] Ao B Y, Xia J X, Chen P H, Hu W Y and Wang X L 2012 *Chin. Phys. B* **21** 026103

[5] Ao B Y, Wang X L, Hu W Y, Yang J Y and Xia J X 2007 *J. Alloys. Comp.* **444–445** 300

[6] Ao B Y, Yang J Y, Xia J X, Wang X L and Hu W Y 2009 *J. Nucl. Mater.* **385** 75

[7] Ao B Y, Ai J J, Gao T, Wang X L, Shi P, Chen P H and Ye X Q 2012 *Chin. Phys. Lett.* **29** 017102

[8] Sun B and Zhang P 2008 *Chin. Phys. B* **17** 1364

[9] Zhu S X, Li R, Yang X W and Xue C R 2003 *Acta. Phys. Sin.* **52** 67 (in Chinese)

[10] Moore K T and van der Laan G 2009 *Rev. Mod. Phys.* **81** 235

[11] Shim J H, Haule K and Kotliar G 2007 *Nature* **446** 513

[12] Butterfield M T, Durakiewicz T, Guziewicz E, Joyce J J, Arko A J, Graham K S, Moore D P and Morales L A 2004 *Surf. Sci. B* **571** 74

[13] Huda M N and Ray A K 2005 *Phys. Rev. B* **72** 085101

[14] McGillivray G W, Knowles J P, Findlay I M and Dawes M J 2011 *J. Nucl. Mater.* **412** 35

[15] Dinh L N, Haschke J M, Saw C K, Allen P G and McLean W 2011 *J. Nucl. Mater.* **408** 171

[16] Islam M F and Ray A K 2011 *Phys. Status Solidi.* **248** 193

[17] Eriksson O, Hao Y G, Cooper B R, Fernando G W, Cox L E, Ward J W and Boring A M 1991 *Phys. Rev. B* **43** 4590

[18] Balasubramanian K, Felter T E, Anklam T, Trelenberg T W and McLean W 2007 *J. Alloys Compd.* **444–445** 447

[19] Haschke J M and Allen T H 2001 *J. Alloys Compd.* **320** 58

[20] Mulford R N R and Sturdy D G 1955 *J. Am. Chem. Soc.* **77** 3449

[21] Haschke J M, Hodge A E and Lucas R L 1987 *J. Less-Common Met.* **133** 155

[22] Ward J W 1983 *J. Less-Common Met.* **93** 279

[23] Bartscher W, Boeuf A, Caciuffo R, Fournier J M, Haschke J M, Manes L, Rebizant J, Rustichelli F and Ward J W 1985 *Physica* **130** 530

[24] Muromuro T, Yahata T, Ouchi K and Iseki M 1972 *J. Inorg. Nucl. Chem.* **34** 171

[25] Ai J J, Liu T, Gao T and Ao B Y 2012 *Comput. Mater. Sci.* **51** 127

[26] Schwartz K and Blaha P 2003 *Comput. Mater. Sci.* **28** 259

[27] Bartscher W 1996 *Solid State Phenom.* **49–50** 159

[28] Qiao Y B, Zhang G H, Li D, Wang J L, Qin X Y and Zeng L 2007 *Chin. Phys. Lett.* **24** 1050

[29] Xie A D, Yan S X, Zhu Z H and Fu Y B 2004 *Chin. Phys.* **14** 1808

[30] Tan M Q, Tao X M, Xu X J and Cai J Q 2003 *Acta Phys. Sin.* **52** 3142 (in Chinese)

[31] de-la Roza A O, Blanco M A, Penáds A M and Luaña V 2009 *Comput. Phys. Commun.* **180** 157

[32] Haschke J M, Allen T H and Morales L A 2000 *Science* **287** 285

[33] Petit L, Szotek Z and Temmerman W M 2003 *Science* **301** 498

[34] Wang Y and Chou M Y 1994 *Phys. Rev. B* **49** 10731

[35] Gürel Y and Eryiĝit R 2009 *J. Alloys Compd.* **447** 478

[36] Wills J O, Ward J W, Smith J L, Kosiewicz S T, Haschke J M and Hodges A E 1985 *Physica* **130** 527

[37] Huiberts J N, Grlessen R, Rector J H, Wijngaarden R J, Dekker J P, de Groot D G and Koeman N J 1996 *Nature.* **380** 231

[38] van Gelderen P, Bobbert P A, Kelly P J and Brocks G 2000 *Phys. Rev. Lett.* **85** 2989

[39] Wu Z G, Cohen R E, Singh D J, Gupta R and Gupta M 2004 *Phys. Rev. B* **69** 085104

[40] Ravindran P, Vajeeston P, Vidya R, Fjellvåg H and Kjekshus A 2006 *J. Power Sources* **159** 88