

**AB INITIO STUDY OF PRESSURE INDUCED
STRUCTURAL, MAGNETIC AND ELECTRONIC
PROPERTIES IN PLUTONIUM PNICTIDES**

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Abstract

We have investigated the pressure induced structural and electronic properties of plutonium pnictides (PuY, Y= P, As, Sb). The total energy as a function of volume is obtained by means of self-consistent tight binding linear muffin-in-orbital (TB-LMTO) method within the local spin density approximation (LSDA). From present study with the help of total energy calculations (spin polarized) it is found that PuP, PuAs and PuSb are stable in NaCl – type structure under ambient pressure. The structural stability of PuP, PuAs and PuSb changes under the application of pressure. We predict a structural phase transition from NaCl-type (B₁-phase) to CsCl-type (B₂-phase) structure for these Pu-pnictides in the pressure range of 20.8 – 42.0 GPa. We also calculate the lattice parameter, bulk modulus, band structure and density of states. From energy band diagram it is observed that all the three compounds exhibit metallic behaviour. The calculated equilibrium lattice parameters and bulk modulus are in good agreement with available experimental data.

Keywords: Structural phase transition; Electronic band structure; Metallic.

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1. Introduction

The rare earth lanthanide and actinide binary compounds exhibit variety of solid state properties due to presence of partially filled f -electrons in these systems. The nature of f -electrons, however, can be changed from localized to itinerant, leading to a variety of changes in their structural, magnetic and electronic properties under the application of pressure [1-2]. The pressure induced structural phase transition in binary compounds of lanthanides and actinides with NaCl-type structure has received considerable attention in the recent past, due to their extensive applications in different fields [3-4]. In the case of actinide compounds, the RE ion has electronic configuration $5f^n (6d7s)^m$. Under the application of the pressure, these compounds lead to structural changes associated with a valance change to $5f^{n-1} (6d7s)^{m+1}$. Since cohesion of solids is crucial, the interionic distance changes as a consequence of the application of pressure. Therefore the delocalization or itinerant behaviour strongly depends on actinide-actinide distance under pressure. Recent studies using synchrotron and powder X-ray diffraction demonstrated that under pressure, a majority of binary compounds with a NaCl-type (B_1) structure undergo a phase transition to CsCl-type (B_2) structure with eightfold co-ordination at high pressure [5-20]. Considerable theoretical but few experimental studies on plutonium binary compounds have been reported during the last few years. In the mono-pnictides of plutonium PuAs shows B_1 to B_2 transition around 35 GPa [1] while PuSb undergoes a B_2 transition at 18 GPa [6]. The structural and elastic properties of PuAs and PuSb compounds have been theoretically studied by Srivastava et al [5], using an interionic potential model approach. No such effort has so far been made in the case of Plutonium phosphide. Moreover, spin polarised and pressure induced electronic structure and its correlation with the structural phase transition in is yet to be explored.

It is well known that with increasing atomic number, the f -shells become smaller and thus are more localized implying a smaller band width [7]. This localization is also favoured from lighter (e.g. P) to heavier anions (e.g. Bi). In this context, it will be interesting as well to investigate spin polarized structural phase transition and electronic properties in PuP and

correlate the same with electronic properties for a few selected Plutonium Pnictides, with fixed atomic number but changing the anion mass (P to Sb).

In the present paper we have investigated, for the first time, the high pressure structural and electronic properties of PuP at ambient and high pressure using *ab initio* Tight Binding-LMTO method within the local spin density approximation (LSDA). Besides, we also report similar results for PuAs and PuSb and compare their structural and electronic properties to visualize how the electronic properties are related to each other in this particular group. In the section 2, we briefly describe the method of total energy calculation which will be followed by results and discussion on structural and electronic properties in section 3.

2. Method of Calculation

The total energy, structural stability, electronic band structure (BS) and density of states (DOS) of three Plutonium pnictides (PuY, Y =P, As and Sb) are calculated in the non-magnetic (NM) and ferromagnetic (FM) states by using the tight binding LMTO (TB-LMTO) method [24-25] within local spin density approximation (LSDA) [26]. Von – Barth and Hedin parameterization scheme [27] has been used for exchange correlation potential, similar to our previous work [23]. The density of states was calculated by tetrahedron method [28]. All the PuY compounds considered here crystallize in B₁-type (NaCl) structure (Space group Fm $\bar{3}$ m, No 225) and stable in ferromagnetic state at ambient pressure. In B₁ structure, Pu atoms occupy (0,0,0) and Y atoms at (0.5, 0.5, 0.5) positions respectively. Since TB-LMTO method works fairly well for closed packed structures and since PuY compounds in NaCl structure are not closed packed, therefore, two equivalent empty spheres were introduced at positions (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75), in such a way that they do not destroy the crystal symmetry [29]. However in the case of CsCl- type structure at high pressure, it being a closed packed one; no such empty spheres were needed. The calculations were performed for 8000 **k**- points (20x20x20 **k**³ grids) in the Brillouin zone for both B₁ and B₂ structures. The E and **k** convergence were checked subsequently. The total energies were calculated by changing the volume from 1.05 to 0.65V₀, where V₀ is the equilibrium cell volume at ambient pressure. The calculated total energies as a function of volume for AnP compounds in B₁ and B₂ structures were fitted to Birch equation of state [30] to obtain pressure – volume(P-V) and pressure-enthalpy (P-H) relations, and finally leading to equilibrium lattice constants (a) and bulk modulus (B) .

3. Result and discussion

3.1. Structural properties

The magnetic stability of PuY compounds has been investigated by estimating the total energy as a function of volume in NaCl structure by performing spin-polarized (FM) and non – spin polarized (NM) calculations. Fig.1 (a-c) shows the calculated total energy of these compounds in FM and NM states. It is revealed from this figure that PuP, PuAs and PuSb are stable in FM state with minimum energy. The structural stability of PuY (Y = As, Sb and P) compounds has been examined by calculating the total energy as a function of volume in ambient (NaCl phase) and at the high pressure (CsCl phase) structures in FM state is plotted in Fig.2 (a-c). Fig 2. clearly indicates that these compounds are stable in B₁ (NaCl) phase at ambient and there is a possibility of structural phase transition to B₂ (CsCl) phase at sufficiently reduced volume (or high pressure). These compounds, as is seen from Fig. 2, transform to CsCl structure on compression. The calculated values of equilibrium lattice constants, in the NaCl phase are 5.51, 5.76, 6.18 Å for PuP, PuAs and PuSb, respectively which agree fairly well with the experimental data [7], shown in Table 1. The structural phase transition is determined by calculating Gibb's free energy (G) for two phases (B₁ and B₂) which is given by $G = E_{\text{tot}} + PV - TS$. Since the theoretical calculations are performed at T= 0K, Gibbs energy becomes equal to enthalpy (H) ($H = E_{\text{tot}} + PV$). For a given pressure, a stable structure is one for which enthalpy has lowest value and the transition pressure (P_t) is determined at which the enthalpies of two structures are the same. Following such a procedure, the phase transition pressures P_t for PuY compounds are calculated for a B₁ – B₂ transition. The phase transition pressures have been estimated as 42 GPa, 37 GPa and 21 GPa, for PuP, PuAs and PuSb with volume collapse of 8.9%, 9.4% and 8.6% respectively. The pressure – volume relationship or equation of states for these compounds are shown in Fig. 3 (a-c). The insets show the variation enthalpy as a function of pressure for respective compounds. In the B₂ phase the corresponding lattice parameters are 3.32, 3.51 and 3.71 Å respectively. In addition to the above structural properties, the values of bulk modulus (B) in both the structures are calculated by using Birch equation of state [30], which has been shown in Fig.3 (for energy as a function of pressure). The calculated results are presented in Table 1 and compared with available experimental results for all the three compounds [5,7,19]. Our calculated values are, however little larger, as compared to the experimental values, the reason being the same as in the case of lattice parameter. However a

more precise measurement might be helpful looking to the uncertainties in the experiment data. No such experimental results in the B_2 phase are reported so far and could not be compared at present.

3.2 Electronic Properties

To understand the electronic properties, we have carried out spin – polarized electronic band structure (BS) and DOS calculations of PuY compounds in both B_1 and B_2 phases. As mentioned earlier, these compounds are metallic ferromagnet. We therefore, have plotted the band structures and density of states in majority and minority spin channels at ambient (B_1 phase) as well as at high pressure (B_2 phase). An exact understanding of the electronic structure of PuY compounds is an extremely challenging problem, because of the itinerant behaviour of their 5- f electrons. However a qualitative picture of their electronic properties can be drawn by comparing the same different pnictides of Pu-element. We have, therefore, calculated the electronic band structure (BS) and density of states (DOS) of three PuY compounds in their B_1 and B_2 phases and plotted them in Figs. 4(a-c) and 5(a-c), where the solid line represents the BS and DOS of majority spin while dotted line represents BS and DOS for minority spin at ambient pressure. The Fermi level is shown by single horizontal dotted line and is set to zero. It is seen from Fig 4 that the PuY compounds are metallic in nature in B_1 phase at ambient, and the region around Fermi energy is densely populated by Pu- d and f - bands .To understand the band structure of PuY qualitatively, in Figs 6 to 8, we have plotted the partial density of states (P-DOS) . These figures reveal that lowest bands around -1.4Ry. are due to Pu- s bands which hybridize with Y- s bands in all the three pnictides . The Pu- d band is quite broad and spread over the energy interval -0.75 to 1.0 Ry. highly localized Pu- f band, stays above the Fermi level, at ambient and moves marginally towards Fermi level on application of pressure (not shown in P-DOS for B_2 phase).



4. Conclusion

The structural phase transition due to high pressure and electronic properties of PuY compounds have been studied using TB-LMTO method. All the three compounds undergo a structural phase transition to B2 structure at 37, 29 and 24 GPa, respectively. All the compounds are found to be metallic in both the phases.

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Table 1: Calculated equilibrium lattice parameter a_0 (Å), bulk modulus B_0 (GPa.), phase transition pressure P_t (GPa), Magnetic moments μ_B and relative change in volume at transition pressure of PuP, PuAs and PuSb in B_1 and B_2 Phases.

Solids	Lattice Constant (Å)		Bulk Modulus B_0 (GPa)		Magnetic moment (μ_B)		Phase Transition Pressure (GPa)	Relative Volume Change (at Pt) %
	B_1	B_2	B_1	B_2	B_1	B_2		
	PuP							
Present	5.51	3.32	146.2	112.6	4.8	4.9	42	8.9
Experimental	5.55 ^a	---	---	---	---	---	---	---
Other	---	---	---	---	---	---	---	---
PuAs								
Present	5.767	3.51	63.9	56.2	4.5	5.01	37	9.4
Experimental	5.88 ^a	---	---	---	---	---	35-38 ^c	9.0 ^c
Other	5.84 ^b	---	69 ^b	---	---	---	35 ^b	8.6 ^b
PuSb								
Present	6.187	3.75	64.9	60.0	5.01	5.5	21	8.6
Experimental	6.241 ^a	---	---	---	---	---	20 ^c	9.0 ^c
Other	6.34 ^b	---	68 ^b	---	---	---	20.8 ^b	6.9 ^b

^a Ref.[7]
^b Ref. [5]
^c Ref [19]



Figure Caption

- Fig.1. Variation of total energy of PuP(a), PuAs(b) and PuSb(c) with relative volume in ferromagnetic and non-magnetic states in B_1 phase.
- Fig.2. Variation of total energy of PuP(a), PuAs(b) and PuSb(c) with relative volume in B_1 and B_2 phases.
- Fig 3. variation of enthalpies in B_1 and B_2 structures, and Pressure volume relation for PuP(a), PuAs(b) and PuSb(c).
- Fig 4. Band structure and Total DOS of ferromagnetic PuP(a), PuAs(b) and PuSb(c) at ambient pressure. Solid lines represent majority spin, dotted lines represent minority spins.
- Fig 5. Band structure and Total DOS of ferromagnetic PuP(a), PuAs(b) and PuSb(c) at high pressure. Solid lines represent majority spin, dotted lines represent minority spins.
- Fig 6. The partial density of states for PuP at the ambient pressure; Solid lines represent majority spin, dotted lines represent minority spins.
- Fig 7. The partial density of states for PuAs at the ambient pressure; Solid lines represent majority spin, dotted lines represent minority spins.
- Fig 8. The partial density of states for PuSb at the ambient pressure; Solid lines represent majority spin, dotted lines represent minority spins.





Figure 1

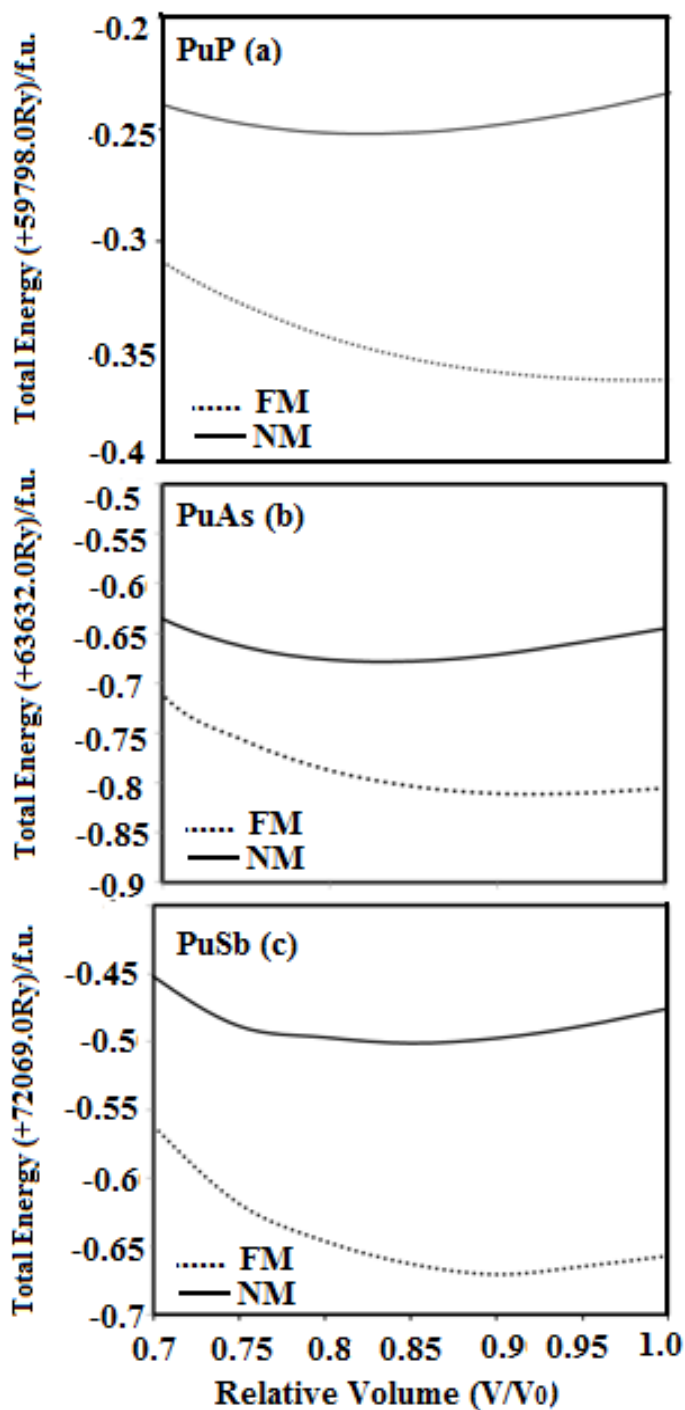


Figure 2

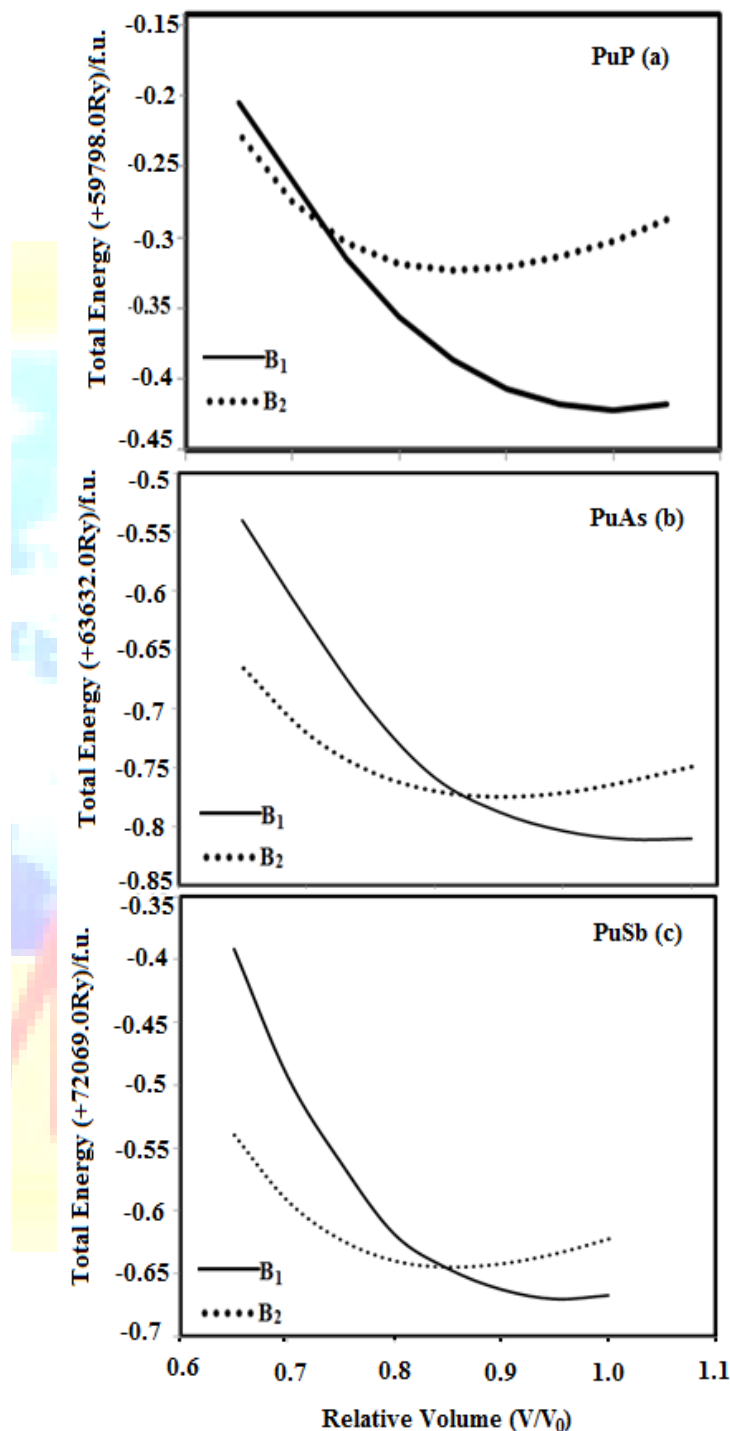


Figure 3.

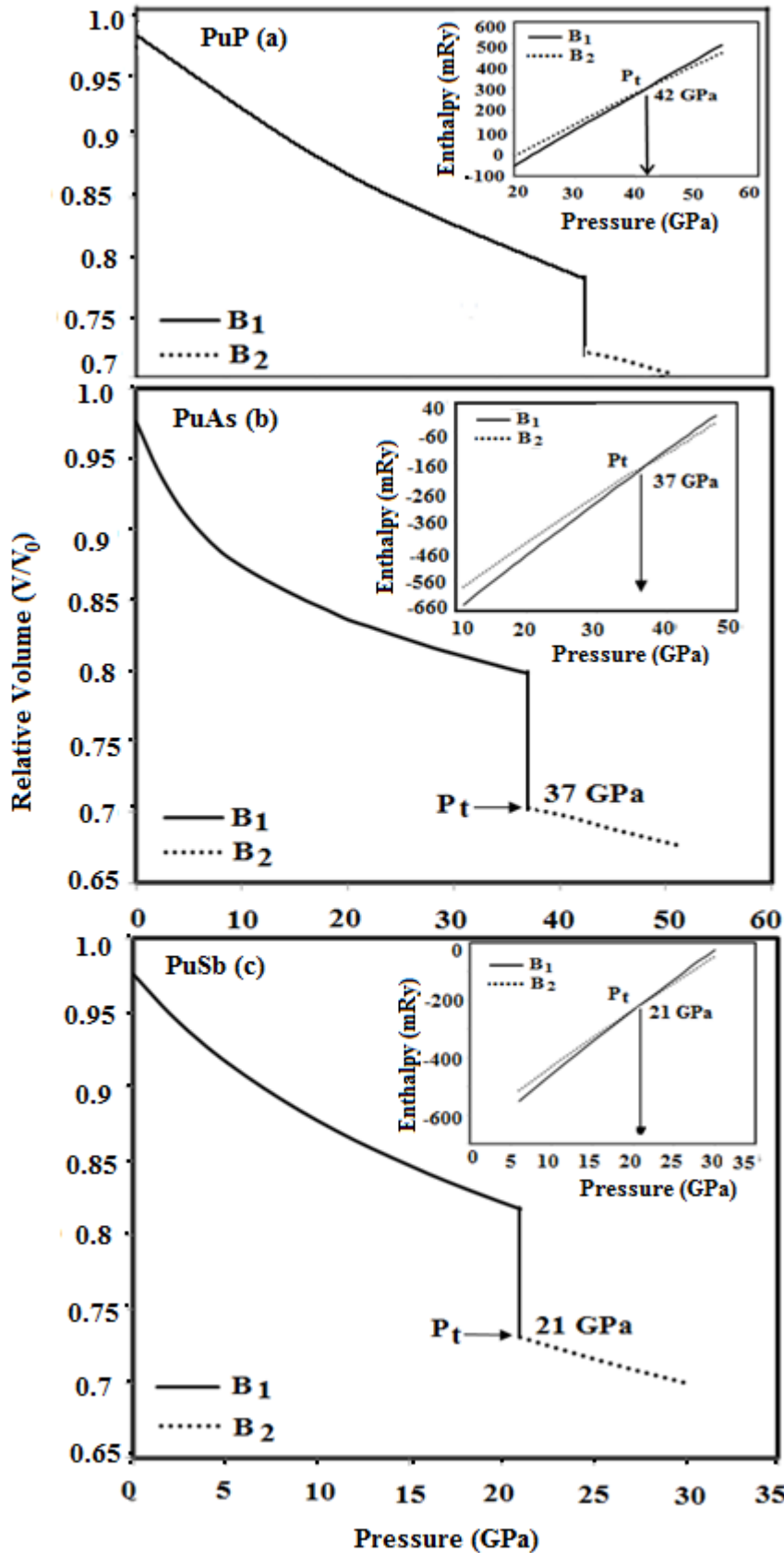


Figure 4

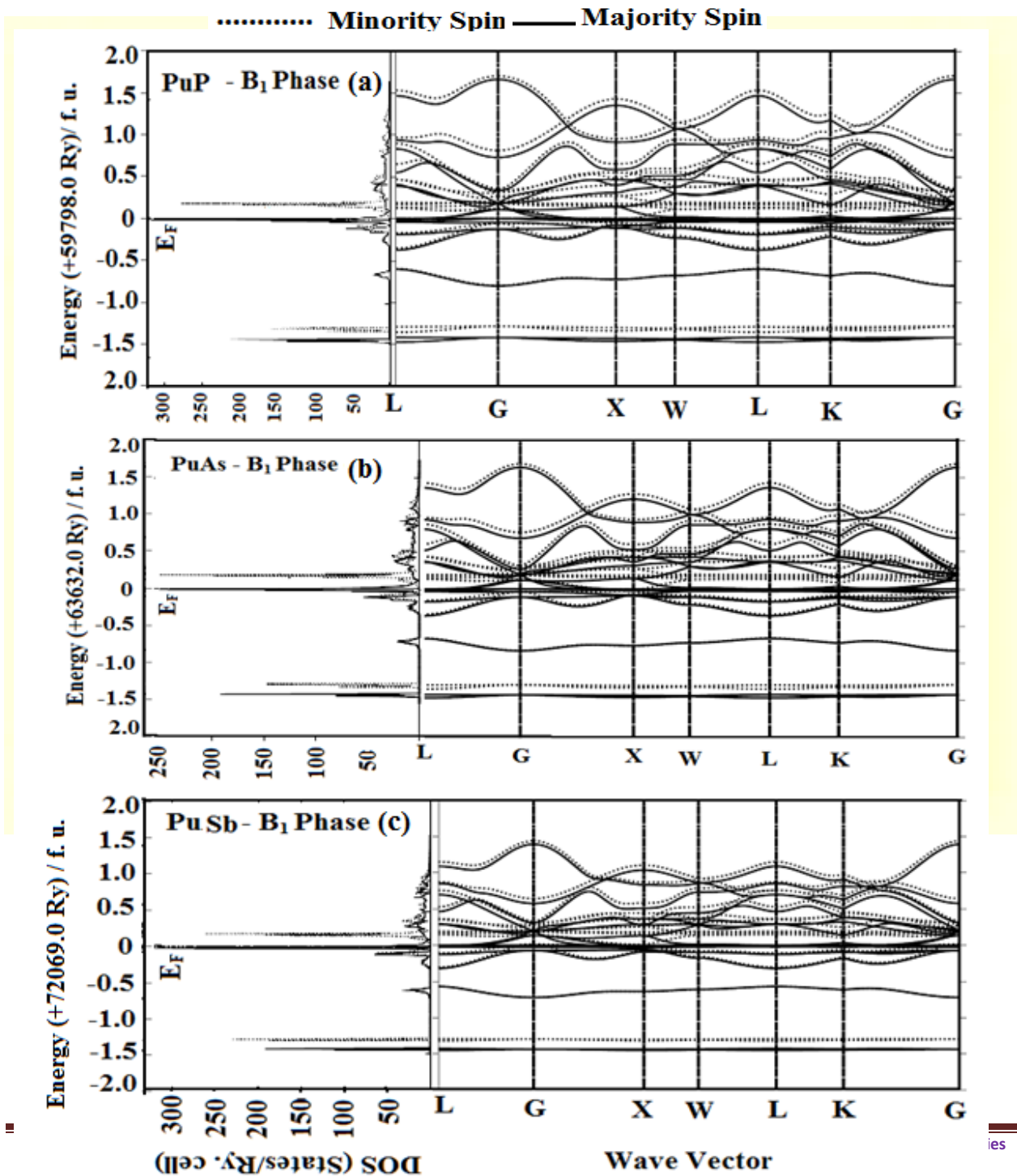
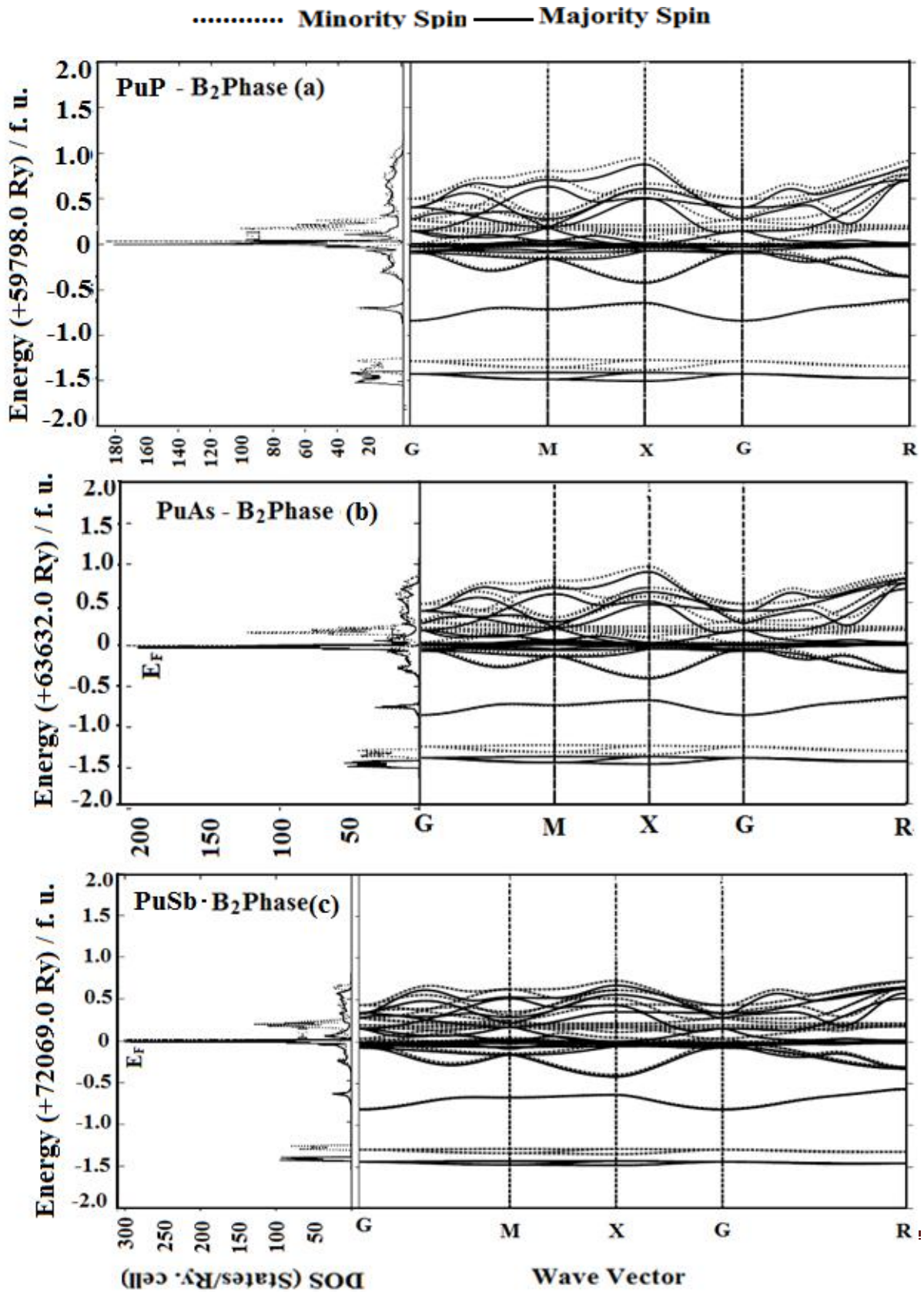


Figure 5



AQ



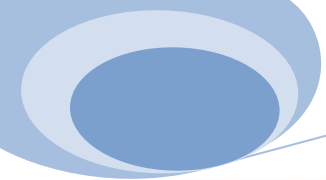


Figure 6

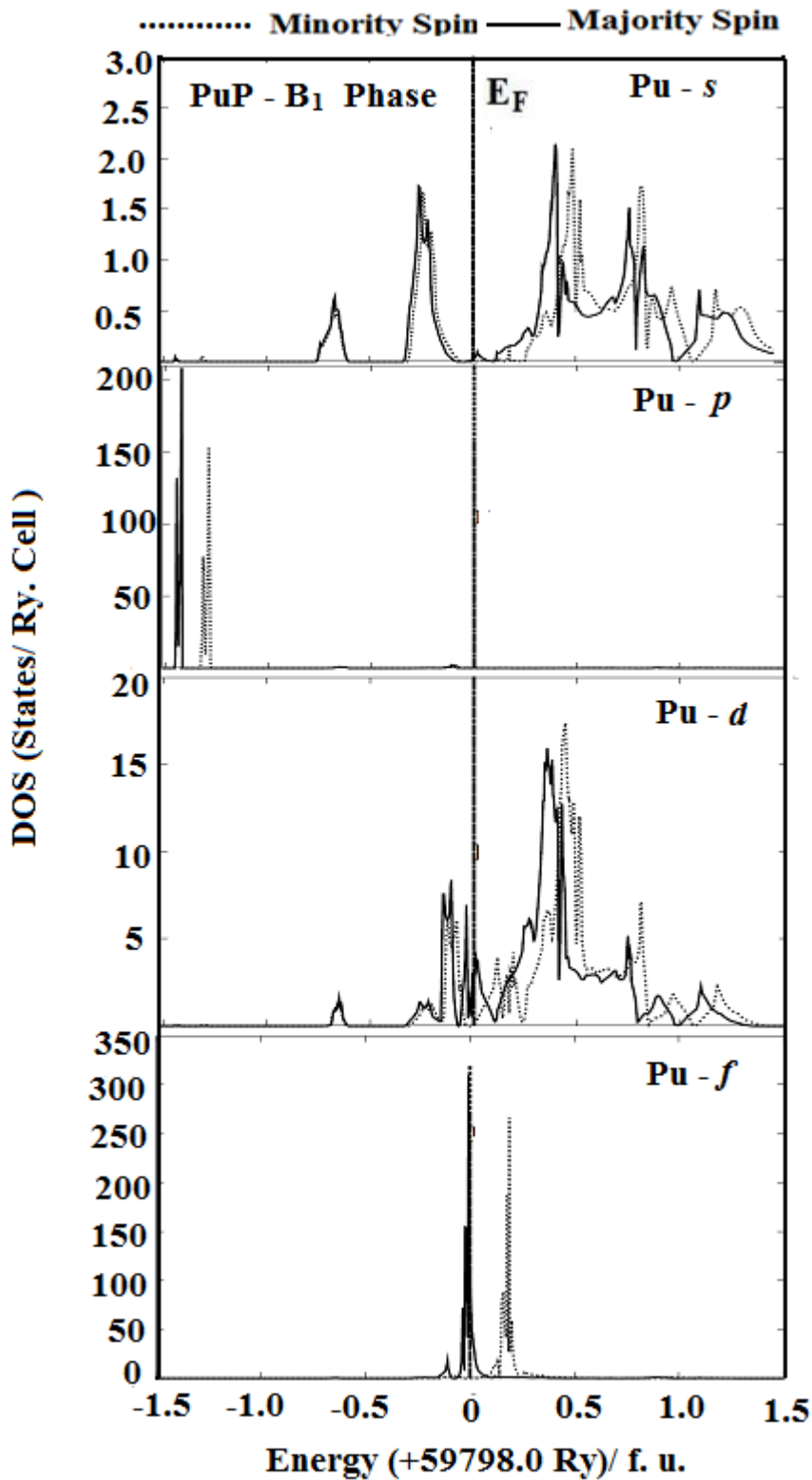




Figure 7

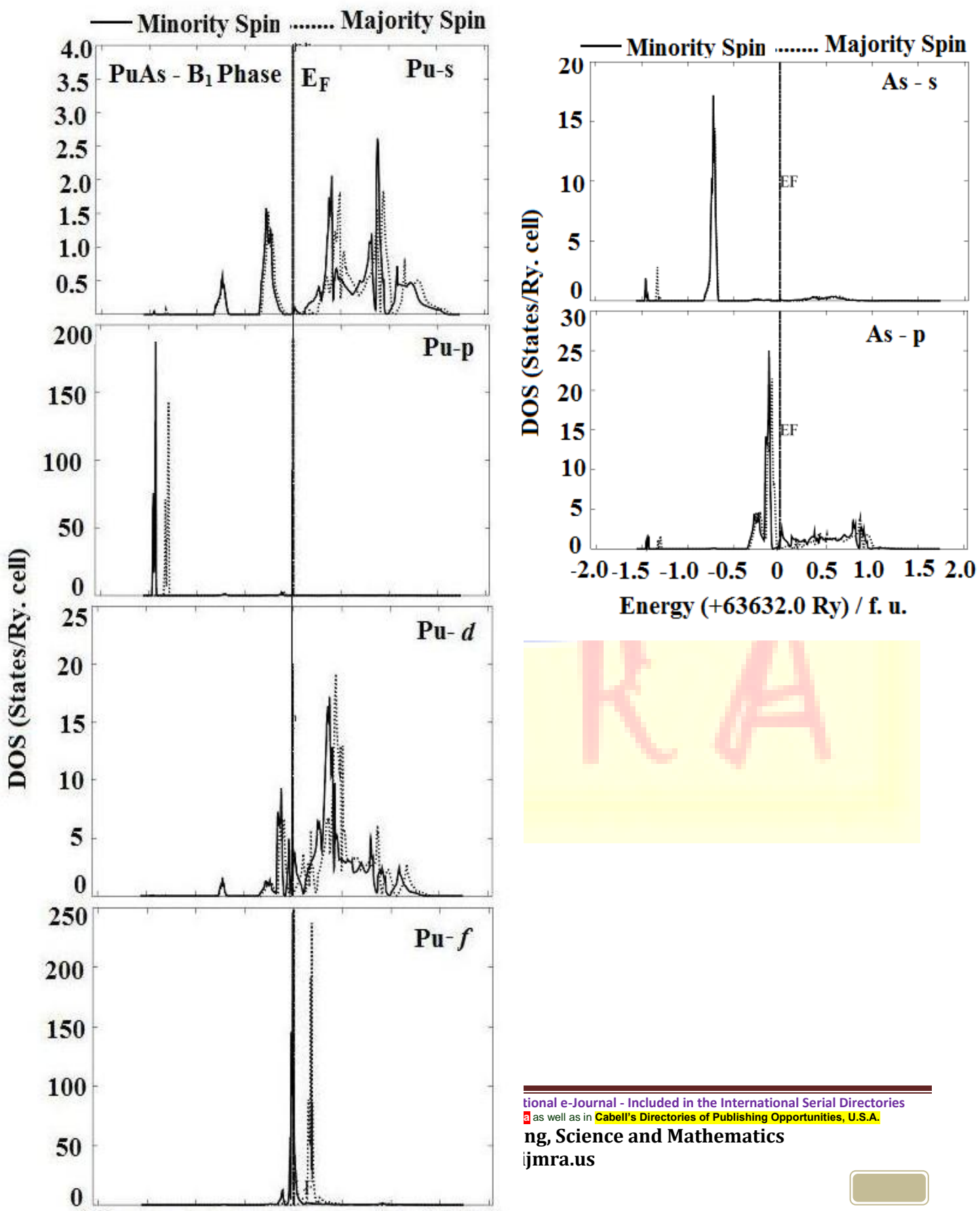




Figure 8

