

EFG AND MAGNETIC STUDIES OF ACTINIDE–POST TRANSITION METALS



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Abstract

In this thesis, we explore the structural and magnetic properties as well as electric field gradient (EFG), hyperfine field (HFF) and quadrupole coupling constant in actinide digallides AcGa_2 ($\text{Ac}=\text{U, Np, Pu}$), NpPx_3 ($\text{Px}=\text{Al, In, Ga}$) and UX_3 ($\text{X}=\text{In, Tl, Pb}$) by using local density approximation (LDA), generalized gradient approximation (GGA) with onsite Hubbard potentials LDA+U and GGA+U and Hybrid Wu-Cohen GGA (HF-WC). The hexagonal AB_2 type AcGa_2 and cubic AuCu_3 type NpPx_3 as well as UX_3 compounds are optimized. The lattice constants, bulk moduli, optimized volumes and ground state energies of these compounds are evaluated from the optimized structures. Our results show that the calculated values of these structural parameters are consistent with the available experimental results. The magnetic structures of the materials under study are investigated by calculating the ferromagnetic, antiferromagnetic and non magnetic phase energies. The UGa_2 , NpGa_2 and NpPx_3 have lowest energies in ferromagnetic phase while PuGa_2 and UX_3 prefer in antiferromagnetic phase, which is in agreement with the experimental results. Due to the 5f- electronic states in these compounds spin orbit coupling (SOC) effect has been considered to include. The spin, orbital and total magnetic moment at U, Np and Pu sites have been calculated computationally with the presence and absence of SOC. Our calculated magnetic moments at uranium, neptunium and plutonium sites are consistent with the experimental values. The orbital, dipolar, Fermi contact as well as total hyperfine and its origin in actinide as well as post transition atomic sites have been investigated for the first time in these compounds. The EFG and quadrupole coupling constant of uranium, neptunium and plutonium atom have been calculated and discussed in detail. These properties are mainly originated from f- states at uranium sites while p- states at post transition sites.

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SAJID KHAN

DEDICATED
TO MY CARING PARENTS,
BROTHERS AND SISTERS

List of publications

This thesis consists on the following published and under-review articles

1. Sajid Khan, M. Yazdani-Kachoei, S. Jalali-Asadabadi, Iftikhar Ahmad “Theoretical Studies of Cubic AuCu_3 -type Intermetallic Actinide Compounds NpPx_3 ($\text{Px}=\text{Al}$, Ga , In)” *Journal of Intermetallics* 93, 77–84 (2017).
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List of symbols and abbreviation used in thesis

i.	DC-----	Direct current
ii.	AC-----	Alternating current
iii.	EFG-----	Electric field gradient
iv.	HFF-----	Hyperfine fine field
v.	η -----	Eta
vi.	GPa -----	Giga pascal
vii.	MHz -----	Mega hertz
viii.	LDA -----	Local density approximation
ix.	GGA -----	Generalized gradient approximation
x.	HF -----	Hartree-Fock
xi.	DFT -----	Density functional theory
xii.	SOC -----	Spin orbit coupling
xiii.	B3LYP -----	Lee-Yang-Parr's correlation functional
xiv.	WC -----	Cohen density gradient functional
xv.	γ -----	Gamma
xvi.	3D -----	3 Dimensional
xvii.	2D -----	2 Dimensional
xviii.	DOS -----	Density of states
xix.	T_N -----	Néel temperature
xx.	Å -----	Angstrom
xxi.	ESR -----	Electron spin resonance
xxii.	EPR -----	Electron paramagnetic resonance

xxiii.	NMR	-----	Nuclear magnetic resonance
xxiv.	TDPAC	-----	Time differential perturb angular correlation
xxv.	BO	-----	Born-Oppenheimer
xxvi.	LDA+U	-----	Local density approximation with Hubbard U
xxvii.	GGA+U	-----	Generalized gradient approximation with Hubbard U
xxviii.	PBEsol	-----	Perdew-Burke-Ernzerhof exchange correlation functional
xxix.	B3PW91	-----	Burke- Perdew's correlation functional
xxx.	FP-LAPW+ lo	-----	Full Potential Linearized Augmented Plane Wave plus Local Orbital Method
xxxi.	LAPW	-----	Linearized augmented plane wave method
xxxii.	α	-----	alpha
xxxiii.	β	-----	beta
xxxiv.	<i>U</i>	-----	Uranium
xxxv.	<i>Np</i>	-----	Neptunium
xxxvi.	<i>Pu</i>	-----	Plutonium
xxxvii.	NQR	-----	Nuclear magnetic resonance
xxxviii.	NQCC	-----	Nuclear quadrupole coupling constant
xxxix.	eV	-----	electron volt
xl.	Am	-----	Americium

Chapter 1

INTRODUCTION

Actinides and their compounds are complex and challenging for research from both scientific and technological point of view. The 5f- orbital of actinides exhibits dual nature, as it some time show the properties of 3d- transition elements and in certain cases it exhibits the nature of 4f- lanthanides series. The main reason of duality is the wider radial extension of the 5f- wave function which can cause a rational hybridization with neighboring orbitals [1-3]. The wider extension of actinide 5f- orbitals cause the formation of intermetallic compounds. The actinide series have total 15 elements; the first element of the series is actinium (89) while the last element is lawrencium (103) [4-7]. The actinides and its compounds mostly show intermetallic nature and their contribution was devoted mainly to chalcogenide, actinide pnictides and posts transition metal compounds [8-10].

Actinides and their post transition metals are intermetallic compounds, exhibit a large diversity in their magnetic nature including heavy fermions, Pauli paramagnetism (USi_3 and UGe_3), spin fluctuation (USn_3 and UAl_3), ferromagnetism (UGa_2 , NpGa_2 , NpAl_3 , NpGa_3 , NpIn_3) [11-13], antiferromagnetism (NpSn_3 , UGa_3 , UIn_3 , UTl_3), unconventional superconductivity as well as magnetic and electric hyperfine interactions [14-17].

Actinides post transition metals have been studied by X-rays diffraction and neutron diffraction techniques and reported interesting results [18-20]. The actinide digallide AcGa_2 ($\text{Ac} = \text{U, Np, Pu}$) have hexagonal AB_2 type crystal structure with space group 191 ($\text{P6}/\text{mmm}$). These are magnetic materials and exhibit intermetallic nature. It is observed by X-ray diffraction

techniques, that the lattice constant and c/a ratio increases when one moves from Uranium to plutonium in AcGa_2 series [18-22].

The actinide post transition metals also have AuCu_3 type cubic structure with space group (Pm-3m) or 221 with position of Au (0, 0, 0) and Cu (0.5, 0.5, 0), (0, 0.5, 0.5), (0.5, 0, 0.5). The most familiar and common examples are NpPx_3 ($\text{Px} = \text{Al, Ga, In}$). All these compounds are ferromagnetic in nature. These materials have small magnetic moment at neptunium site. Oddou *et al.* [23] investigated the neptunium magnetic moment in the NpGa_3 and NpIn_3 compounds by various experimental techniques like DC, AC and magnetic susceptibility. The magnitudes of magnetic moments are 1.13 and 1.56 μ_B , respectively. Colineau *et al.* [24] studied NpGa_3 by using Mössbauer spectroscopy and powder magnetization resistivity techniques and concluded antiferromagnetic order at Néel temperature $T_N = 65$ K and observed the transition to a ferromagnetic structure at $T_C = 50$ K, while Zwirner *et al* [25] observed experimentally that NpGa_3 is ferromagnetic under 50 K with magnetic moment of 1.6/Np by different experimental techniques like AC and DC as well as Mössbauer spectroscopy.

Vast experimental literature is available for uranium cubic compounds UX_3 ($\text{X} = \text{In, Tl, Pb}$). It has been investigated by X-ray diffraction techniques that the lattice constant of these cubic compounds increases from indium to lead in UX_3 series. All these materials are anti ferromagnetic in nature with low electronic specific heat. The magnetic moments at uranium site in UX_3 are 1 μ_B , 1.6 μ_B and 1.7 μ_B , respectively. The magnetic moments at uranium site also increases like the lattice constant in UX_3 , which shows a direct relation between lattice constant and magnetic moment [26-29].

NpSn_3 also exhibit AuCu_3 type crystal structure with experimental lattice constant 4.626 Å and bulk modulus 63 GPa. The cubic NpSn_3 is an itinerant-electron anti-ferromagnetic (IAF)

compound. The NpSn_3 exhibits some distinguished properties, like small magnetic moment ($0.28 \mu_B$) with a Néel temperature of only 9.5 K and small electronic specific heat of magnitude $88 \text{ mJ mol}^{-1} \text{ K}^{-2}$ [6, 30-33].

All the actinide and their compounds are heavy fermions in nature. The magnetic properties of actinides exhibit dual character like localized or delocalize. There is either f-f overlapping of actinide elements or a hybridization of f- state with ligand orbital s, p and d-. Hill [34] was the first one to introduce a necessary condition for the localized and delocalized electron of actinide compounds. This condition requires that the An-An inter-ionic spacing must exceed a critical value 3.4 - 3.6 Å for delocalized nature of orbital in an atom. Below this critical spacing, 5f-5f wave function overlap is sufficient to delocalize the 5f- electrons and suppress the formation of stable magnetic moments. As the Ac-Ac spacing exceeds this critical spacing, the delocalizing effect due to f-f overlap is diminished but f-spd hybridization may still prevent the formation of stable local moments. The extensive studies of uranium binary compounds with inter-atomic spacing (U-U) is larger than 3.4- 3.6 Å. Inter-atomic spacing (U-U) gives an opportunity to study the salient features related to magnetic moment formation where f- spd hybridization is the leading factor contributing to the delocalization of the magnetic electrons [35-36].

The Uranium, Neptunium and Plutonium have quadrupole nuclei with spin quantum number $I > 1/2$. The nuclear quadrupole moment of actinides are ^{238}U 3.663, ^{235}U 4.936, ^{237}Np 3.886 and ^{241}Pu 6.0 barn while the post transition metal have ^{70}Ga 0.105, ^{115}In 0.77, ^{187}Tl -2.43 and ^{205}Pb 0.23 barn. The electric field gradient (EFG) interacts to quadrupole moment resulting in wide peak broadening [37-38]. The EFG, HFFs, quadrupole coupling constant (C_Q) and asymmetry parameter (η) of atomic nuclei of actinide compounds AcGa_2 (Ac =U, Np, Pu),

NpPx_3 ($\text{Px} = \text{Al, Ga, In}$) and UX_3 ($\text{X} = \text{In, Tl, Pb}$) are attractive parameters for research in science and technology. These factors compute quadrupole interaction energy, which is a vital analysis approach in condensed matter and nuclear physics. These parameters as well as their wavefunction are helpful to understand the complex molecular structure in biological and chemical sciences [34]. Oddou *et al.* [24] and Zwirner *et al.* [25] experimentally measured the quadrupole coupling constant by Mössbauer spectroscopy and found 105.644, 148.86 and 139.258 MHz and the corresponding EFG at neptunium sites are 1.13, 1.56 and $1.51 \times 10^{21} \text{ V/m}^2$ in NpPx_3 ($\text{Px} = \text{Al, Ga, In}$) family.

Magnetic Hyperfine Field (HFFs) and electric quadrupole interactions have a significant role in understanding the electric quadrupole and environment of electronic cloud around the nucleus. Electric field gradient EFG is also an informative parameter which clearly explains the electric quadrupole interaction energy between nuclear electric quadrupole of the nuclei and extra electric field generated by the electron cloud around the nuclei. EFG is linked to the nuclear electric quadrupole moment (Q) generates an interacting energy which can be measured by using number of spectroscopic methods, such as Nuclear Quadrupole Resonance (NQR), Nuclear Magnetic Resonance (NMR), Mössbauer spectroscopy, Perturbed Angular Correlation (PAC) and Electron Paramagnetic Resonance (EPR). The EFG phenomena arise at the nucleus position due to the surrounding electronic distribution. The EFG is non-zero only if the charge distribution violates the cubic symmetry [37-39].

In this thesis all the computational work is performed by using the full potential linearized augmented plane wave plus local orbital method (FPLAPW + lo) in the framework of Density Functional Theory (DFT). We used different exchange correlation functionals like LDA, GGA and in addition of Hubbard parameter U i.e, LDA+U and GGA+U. The various properties

of the actinide compounds are also calculated by Hybrid Functionals (HF-PBEsol), HF-WC and HF-B3LYP in the absence and presence of Spin Orbit Coupling (SOC).

In this thesis the first chapter presents the introduction and inspiration of the project. In chapter second, the literature review as well as the different types of magnetic materials, electronic specific heat, HFF and EFG are discussed. The information about DFT and wien2k code are discussed in third chapter and the fourth chapter contain results and discussion of our DFT calculations for structural, electronic, magnetic, electronic specific heat, hyperfine field and electric field gradient of post transition metals like, UGa_2 , NpGa_2 , PuGa_2 , NpAl_3 , NpGa_3 , NpIn_3 , UIn_3 , UTl_3 and UPb_3 . The whole project is summarized in the last chapter.

Chapter 2

LITERATURE REVIEW

2.1 Magnetic Materials

Magnetism is one of the fundamental property of a material which has extensive application in science and technology. Magnetism usually arises in a material due to the spinning and orbital motion of electrons as well as their interaction [38-40]. On the basis of response of magnetic materials to external magnetic field they are classified into the following groups;

- (a) Diamagnetic Materials
- (b) Paramagnetic Materials
- (c) Ferromagnetic Materials
- (d) Antiferromagnetic Materials

The opposition of magnetic moment of certain medium to external magnetic field is known as diamagnetism. When magnetic field is applied to a diamagnetic material a magnetic flux change is produced as a result of induced magnetic moment which opposes the external field under the Lenz law. The diamagnetic materials have usually even number of electrons in their outer most shell. These materials have negative magnetic susceptibility and small magnitude of permeability. The most common examples of diamagnetic elements in periodic table are copper, silver and mercury [39, 40].

Paramagnetic materials are weakly attracted by external magnetic field. Paramagnetic materials have some magnetic moment at the atomic level due to the unpaired electrons in the

outermost shell. Generally, these atoms have random magnetic moments which are aligned to external magnetic field and produce positive magnetization as well as magnetic susceptibility. The magnetization comes to zero when the external fields remove. The most common examples are Oxygen, Titanium and magnesium [41].

All the Ferromagnetic materials have large number of domains which consist on magnetic dipole moment. The dipole moments of these materials are aligned in the presence of external magnetic field. These materials have large positive magnetic susceptibility. The ferromagnetic materials convert to paramagnetic at specific temperature which is known as Curie temperature. The commonly known examples of ferromagnetic materials are iron, cobalt and nickel [42-43].

Antiferromagnetism are the other interesting and fundamental magnetic materials. The magnetic moment of antiferromagnetic material cancels the effect of each other and leads to net zero magnetic moment of it. The magnetic nature of antiferromagnetic material was calculated indirectly by number of experimental techniques like, magnetic susceptibility and specific heat techniques. Shull and Smart introduced neutron diffraction technique and measured magnetic moment of antiferromagnetic materials for the first time in year 1949 [44].

A group of other researchers also studied the spin structure of different manganites by using neutron scattering techniques [45-46]. On the basis of the direction of the magnetic moment the antiferromagnetic materials are divided into three known groups, i.e like G-type, C-type and A-type AFM. The most familiar examples are Chromium, Nickel Oxide (NiO) and Iron manganese (FeMn) [47].

2.2 Intermetallic Actinide Post Transition Properties

The actinide elements exist in different composition with post transition metals. The different Actinide combinations are AcX , AcX_2 and AcX_3 ($\text{Ac} = \text{U, Np, Pu}$) while ($\text{X} = \text{Ga, In, Tl, Sn, Pb, Bi}$). AcX_2 ($\text{Ac} = \text{U, Np, Pu}$ and $\text{X} = \text{Ga}$) crystallizes in the hexagonal AB_2 -type structure. Actinide digallide AcGa_2 [$\text{Ac} = \text{U, Np, Pu}$] are intermetallic hexagonal AB_2 type crystal materials. The general 3D- and 2D- crystal structures of AcGa_2 are shown in Figs. 2.1 and 2.2. The position of actinides are Ac (0, 0, 0), Ga ($1/3, 2/3, 1/2$) and ($2/3, 1/3, 1/2$) with space group 191 or P6/mmm [12, 48, 50]. The X-ray diffraction study of UGa_2 confirms that there is an orthorhombic distortion below 100 K. In external magnetic field it exhibits ferromagnetic structure with Curie temperature $T_c = 125$ K. Andreev *et al.* [49] used different experimental techniques like magnetic susceptibility as well as neutron diffraction and found out the magnetic moment at Uranium site which magnitudes as $3.0 \mu_B/\text{U}$ and $2.7 \mu_B/\text{U}$ respectively.

The large magnetic moment at Uranium site claimed due to the localized electron at Uranium site of 5f- electrons [12, 50]. Yaar *et al.* [13] experimentally observed the magnetic moment of NpGa_2 . The magnetic and electronic properties of NpX_2 ($\text{X} = \text{Ga, Si}$) were studied by various techniques like AC, DC and Mössbauer magnetization techniques. The NpGa_2 exhibits ferromagnetic order with $T_C = 55(5)$ K. The magnetic moment at Neptunium site is $\mu_{\text{orb}} = 2.39 \mu_B$ [51-52]. The calculated structural, electronic as well as magnetic properties of AcX_2 have been tabulated as shown in Table 2.1, Boulet *et al.* [20] examined the magnetic properties of PuGa_2 using specific heat magnetization technique and magnetic susceptibility and found the antiferromagnetic structure. The Néel temperature of PuGa_2 is $T_N = 74$ K. The antiferromagnetic order in PuGa_2 is very strong and it is not affected by magnetic fields up to 9 T. The electronic specific heat of PuGa_2 is $\gamma = 12 \text{ mJ mol}^{-1} \text{K}^{-2}$ [20].

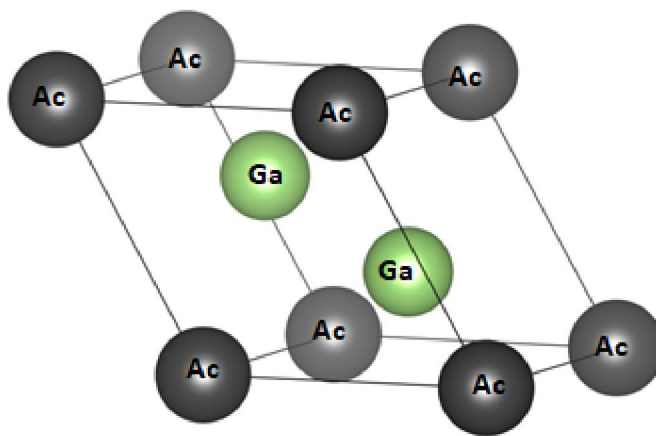


Figure. 2.1: The 3D crystal structure of AcGa_2 ($\text{Ac}=\text{U}, \text{Np}, \text{Pu}$), where the corner atom show Ac (U, Np, Pu) and the other Ga atom. The atomic positions of Ac (U, Np, Pu) are $[0, 0, 0]$ while position of Ga are $[1/3, 2/3, 1/2]$ and $[2/3, 1/3, 1/2]$ [12, 48, 49, 51].

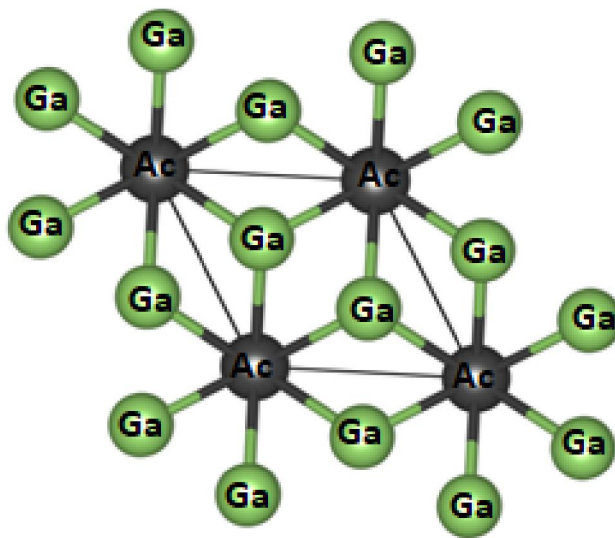


Figure 2.2: The 2D crystal structure of AcGa_2 , where black stand for Ac ($\text{Ac}=\text{U}, \text{Np}, \text{Pu}$) while other show gallium atom [12, 48, 49, 51].

Table 2.1 Characteristic properties of UX_3 and NpX_3 , with lattice constant ($\text{\AA}$), magnetic transition temperature T_{mag} (K) with electronic specific heat coefficient γ ($\text{mJmol}^{-1} \text{K}^{-2}$).

	UGa ₂ [18, 20, 54]	NpGa ₂ [13, 18, 20,54]	PuGa ₂ [15,18,20,54-55]
Lattice constant ($\text{\AA}$)	a=b= 4.21, c=4.01	a=b=4.259, c=4.077	a=b=4.254, c=4.124
An–Ga distances ($\text{\AA}$)	3.150	3.190	3.210
c/a	0.95	0.96	0.97
Magnetic structure	Ferromagnetic	Ferromagnetic	Antiferromagnetic
T_c/T_N	125.0 K	55.0 K	74.0 K
μ_{order} (μ_B)	2.7	2.39	0.42
γ ($\text{mJ mol}^{-1} \text{K}^{-2}$)	11		12

The small electronic specific heat exhibits the low DOS around the Fermi level [53-56]. The second important family of actinide post transition metal is AcX_3 ($Ac = U, Np, Pu, X = Al, Ga, In, Tl, Sn, Pb, Bi$). All these compounds exhibit cubic $AuCu_3$ type structure. $NpPx_3$ [$Px = Al, Ga, In, Tl, Sn, Pb, Bi$] intermetallic compounds exhibit $AuCu_3$ type cubic crystal structures with space group $Pm-3m$ (221), the atomic positions of Ac at the origin while Cu on the six faces of unit cell [57-58]. The cubic crystal structures are shown in figure 2.3 and 2.4. These compounds are excellent nominee for an investigation of 5f- hybridization in actinide materials.

The other important series of actinides is UX_3 ($X = Ga, In, Tl, Sn, Pb, Bi$). This series also has $AuCu_3$ type crystal structure. The high quality crystal of UIn_3 has been prepared by the self- efflux method. There are numerous experimental works like, de Haas-van Alphen (dHvA) oscillation, specific heat, magnetic susceptibility; electrical resistivity and Mössbauer spectroscopy have been reported for these compound [59-63]. The UIn_3 exhibit the antiferromagnetic structure with the Néel temperature $T_N=88K$.

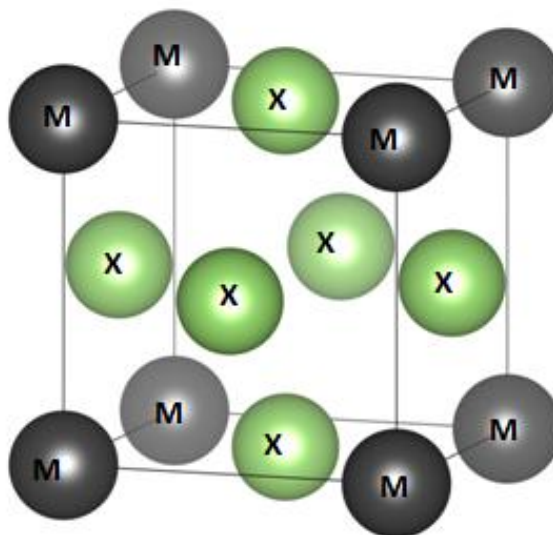


Figure. 2.3: 3D AuCu₃ type crystal structure of MX₃ (M =U, Np, X =Al, In, Ga, Tl, Pb), where the corner atom shows uranium or neptunium with atomic positions (0, 0, 0) while face atoms are Al, In, Ga, Tl, Pb with position of X (0.5, 0.5, 0.0), (0.5, 0.0, 0.5) and (0.0, 0.5, 0.5) [23, 60, 61].

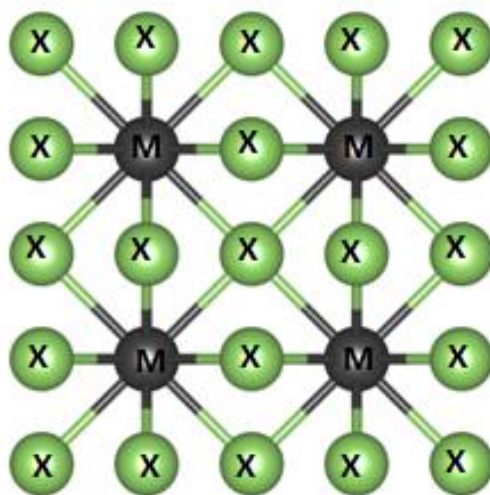


Figure 2.4: 2D crystal structure of AuCu₃, where black stands for M (M=U, Np) and X stands for (X= Al, Ga, In, Tl, Pb) [23, 60, 61].

This material is antiferromagnetic in nature with magnetic moment $1 \mu_B /U$. The magnetic moment as well as electronic specific heat of UTl_3 and UPb_3 have been studied. All these materials are anti ferromagnetic in nature. The magnetic moment is increased from 1.6 to $1.7 \mu_B$. USn_3 is the other important compound of $AuCu_3$ family. USn_3 has Pauli paramagnetic and spin fluctuation property. The USn_3 has large specific heat (169 mJ/mol.K^2) which means that large number of density of states occur at Fermi level [14, 16-17]. The $NpAl_3$ crystals have been studied by X-ray diffraction techniques and its lattice constant is measured as $4.261(1) \text{ \AA}$. The magnetic properties of $NpAl_3$ have been studied by neutron diffraction method, which exhibits the antiferromagnetic nature with the Np magnetic moment of $1.3 \mu_B$ and $T_N = 73 \text{ K}$ [23, 27, 64-66]. The $AuCu_3$ type cubic post transition metal compounds $NpGa_3$ has a Néel temperature $T_N \approx 65 \text{ K}$. The antiferromagnetic first order transition to ferromagnet has been observed. The Curie temperature of $NpGa_3$ is $T_c \approx 50 \text{ K}$ by Mössbauer measurement and neutron diffraction techniques. The saturation Np moment was found $1.56 \mu_B$ and a moment jump to $\approx 0.2 \mu_B$ from F-AF transition [21, 24, 67-70]. The single crystals of $NpIn_3$ have been prepared by the In-flux method. The specific heat, magnetic moment and electrical resistivity studied and it is found that $NpIn_3$ is ferromagnetic and first order transition to antiferromagnetic has been observed at $T_N = 10 \text{ K}$. The magnetic moments of Np in $NpIn_3$ have been investigated by number of researchers. The $NpIn_3$ have antiferromagnetic nature with magnetic moment $1.4 \mu_B$ [22, 71-72]. In Addition to uranium and neptunium the plutonium also has large electronic specific heat and antiferromagnetic structure [14, 20, 73]. The electronic specific heat, structural and magnetic structures are presented Table 2.2.

Table 2.2. Characteristic properties of UX_3 and NpX_3 , cited from refs [14-17, 22, 62-64, 71] Lattice constant ($\text{\AA}$), magnetic transition temperature T_{mag} (K) with electronic specific heat coefficient γ ($\text{mJmol}^{-1} \text{K}^{-2}$).

	Lattice constant ($\text{\AA}$)	Magnetic structure	T_{mag} (K)	γ
UAl_3	4.265	Paramagnetic		47
UGa_3	4.248	Antiferromagnetic	$T_N = 67$ (K)	52
UIn_3	4.601	Antiferromagnetic	$T_N = 88$ (K)	40
UTl_3	4.674	Antiferromagnetic	$T_N = 90$ (K)	
USn_3	4.626	Paramagnetic		170
UPb_3	4.793	Antiferromagnetic	$T_N = 32$ (K)	110
$NpAl_3$	4.266	Antiferromagnetic	$T_N = 37$ (K)	
$NpGa_3$	4.243	Antiferromagnetic	$T_N = 65$ (K)	
$NpIn_3$	4.619	Antiferromagnetic	$T_N = 08$ (K)	72
$NpTl_3$	4.674	Antiferromagnetic	$T_N = 30$ (K)	
$NpSn_3$	4.626	Antiferromagnetic	$T_N = 9.5$ (K)	88

2.3 Hill Criteria

The actinides and their intermetallic compounds show complex magnetic nature due to 5f electrons. It shows dual nature and covers a wide range of magnetic properties varying from itinerant band like character (3d elements) to localized behaviour (typical for 4f elements). The extensive variety of 5f- electrons mostly a result of the broad wave function of the 5f- electrons as compared to 4f lanthanide [1,74-75]. This broad extension leads to two different overlapping of 5f electrons, either with neighboring actinide atom or strong hybridization with alloying partner. It was first noticed by Hill [34, 76] that one critical parameter investigating the magnetic nature of actinide atoms and their compounds is the Ac-Ac gap. If the Ac-Ac separation is less than a critical value ("Hill limit"), the 5f- electrons approach to delocalization such that magnetic order can no longer be maintained due to direct overlapping of 5f-5f orbitals. At large actinide-actinide partition, however, 5f delocalization is only probable by hybridization with ligand

orbitals (f-sp_d). The actinide AcX₃ materials, where X is a non-transition element from group III-A or IV-A, exhibit the cubic AuCu₃ type crystal structure. These compounds have Ac-Ac separation equal to the lattice constant of the unit, although the inter atomic distance far away above from critical Hill limit, hence the delocalization in such compounds lead by hybridization of 5f- electrons with ligand electrons [74]. The UX₃ compounds do not order magnetically (X = Al, Si, Ge, Sn) or they exhibit an antiferromagnetic structure (X = Ga, In, Tl, Pb). From this nature it is obvious that by decreasing the atomic size of X atom the 5f- hybridization to the ligand increases, furthermore, the hybridization between f- and p- states show dominant nature due to the large number of p- orbital in group IVA compared to II-A and III-A [74]. A similar trend is also observed for the NpX₃ relatives [22, 34, 77-78]. On the other hand, the NpX₃ compounds are more magnetic than UX₃ compounds due to the less extended neptunium 5f wave functions. For uranium and neptunium the Hill limits are $\approx (3.25 - 3.5 \text{ \AA})$. The Hill limit of certain neptunium cubic Laves phase compound has been studied by application of external pressure in Mössbauer experiment and pointed out that the 5f- delocalization reduces with decreasing volume [14, 27, 79-82].

2.4 Electric Field Gradient (EFG)

Electric field gradient is a second rank tensor defined by the following traceless tensor

$$V_{mn} = \frac{\partial^2 V}{\partial x_m \partial y_n} = \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix} \quad 2.1$$

where V is the classical electrostatic potential at the nucleus site, V_{xx}, V_{yy} and V_{zz} are the components of the diagonalized electric-field gradient (EFG) tensor in cartesian coordinate with the convention

$$|V_{xx}| \geq |V_{yy}| \geq |V_{zz}|$$

The informative component of EFG is V_{xx} , V_{yy} and V_{zz} . The total V_{zz} which is the principal component of EFG can be calculated by the sum of its lattice and valence contributions:

$$V_{zz}^{total} = V_{zz}^{val} + V_{zz}^{latt} \quad 2.2$$

where the resultant EFG is due to the non spherical charge distribution or valence EFG (V_{zz}^{val}) at atomic site and interstitial region or lattice EFG (V_{zz}^{latt}). The V_{zz} can be expanded inside the muffin-tin sphere as

$$V_{zz} = \lim_{r \rightarrow 0} \left[\frac{5}{4\pi} \right]^{1/2} \left[\frac{V_{20}(r)}{r^2} \right] \quad 2.3$$

Equation (2.3) exhibits principal component of EFG tensor along z-direction and radial component (V_{20}) can be computed as;

$$V_{20}(r = 0) = \frac{4\pi}{5} \int_0^{R_{MT}} \frac{\rho_{20}}{r} dr - \frac{4\pi}{5} \int_0^{R_{MT}} \frac{\rho_{20}}{r} \left(\frac{r}{R_{MT}} \right)^5 dr + 4\pi \sum_k V(k) J_2(kR_{MT}) Y_{20} \quad 2.4$$

where the primary term in equation (2.4) is due to the quasi-core or valence EFG in muffin-tin sphere while other terms are due to the interstitial region, while $J_2(kR_{MT})$ is the spherical Bessel function in the muffin-tin sphere [83-85]. The quadrupole nuclei with spin quantum number have $I \geq 1$ has non zero nuclear quadrupole moment. The nuclei $I > \frac{1}{2}$ interact to electric field gradient as a result quadrupole interaction energy arises

$$E = \frac{V_{zz}e^2Q}{h} \quad 2.5$$

This relation also shows the connection between condensed matter to the nuclear physics, where e is electronic charge in coulomb, Q shows nuclear quadrupole moment of nuclei in barn (10^{-28} m^2), h is Plank constant in J.S and E is the interaction energy of Q and EFG. The EFG also predicts the distribution of electrons around the nuclei.

The η exhibits the deviation of electron cloud from spherically symmetry. The asymmetry parameter takes values from 0 to 1. The asymmetry parameter η is defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad 2.6$$

The zero value of η exhibits spherical distribution of electrons around the nucleus: while non-zero shows non-spherical distribution. The value of EFG of an atom varies from compound to compound. It means it behaves like a finger print in materials. The interaction frequency which is also called quadrupole coupling constant can be expressed as

$$C_Q = \frac{eQV_{zz}}{h} \quad 2.7$$

The magnitude of such frequency is usually in range of MHz. The perturbed-Angular Correlations (PAC), Mössbauer Spectroscopy, (NMR) and (NQR) are experimental tools to measure C_Q which gives local information about the interaction of probe-nucleus to the environmental electronic distribution.

The EFG tensor is linearly connected to the asphericity of the electronic charge density near the probe sites and the quadrupole coupling constant $C_Q = \frac{eQV_{zz}}{h}$ predicts the nature of covalency or

ionicity of chemical bonds in a solid material. Although nuclear quadrupole moment is a purely nuclear quantity and for quadrupole nuclei the Q is evaluated only with limited accuracy and its investigation is still an active field for researchers. The famous possible technique to determine Q is to use the experimental C_Q and computational EFG, but the computational EFG calculations are difficult due to the strong dependence on surrounding charge distribution.

In calculated results, small variation in the order of 0.01 electrons in a given orbital leads to quite unusual EFG outcomes, that's why the EFG calculation is a difficult job and needs a very good description of electronic structure. In the pioneering work, Blaha *et al.* [86] demonstrated that the Linearized Augmented Plane Wave band-structure method (LAPW) for calculation of EFG is most reliable approach [87].

In addition, this technique proved to be both accurate and satisfactory to determine nuclear-quadrupole moments Q of even quite heavy nuclei (U, Np, Pu). An understanding of such measurements can lead to a comprehensive knowledge of structural, magnetic, electronic as well as chemical bonding nature of materials [88-91]. Errico *et al* investigated for the first time EFG at indium site by using LDA and GGA approach which are 2.45×10^{21} and 2.39×10^{21} V/m² [92]. The experimental quadrupole coupling constant for ¹¹⁴In, ¹¹⁵In and ¹¹⁷In by using different experimental approaches are 8.4 MHz, 45.24 MHz and 32.1 MHz. Using both computational and experimental data the computed magnetic moments are $Q(^{114}\text{In}) = 0.14$, $Q(^{115}\text{In}) = 0.77$ and $Q(^{117}\text{In}) = 0.64$ b. The calculated Q values are close to the experimental outcome, which show the reliability of the theoretical techniques [93-96].

2.5 Magnetic Hyperfine Field

The hyperfine field is a very informative parameter in atomic and condensed matter physics. The hyperfine interaction arises due to the magnetic moment of electrons with nuclei magnetic moments. This type of interaction causes the (ESR) or (EPR) and NMR spectra at the atomic sites. The interaction of hyperfine field and electric field gradient gets some remarkable concentration in heavy compounds. This type of interaction can be evaluated by numerous experimental methods, like time differential perturbed angular correlation (TDPAC), Mössbauer spectroscopy and NMR [47, 97]. The HFF consists of Fermi contact, dipolar and orbital components. Fermi contact further splits into the core and valence contributions. Hyperfine field of specific nuclei of an atom can be written as

$$B_{hf} = B_{Dipolar} + B_{Fermi} + B_{Orbital} + B_{Lattice} \quad 2.8$$

where $B_{Dipolar}$ is the dipolar field contributed by electrons spin density, $B_{Orbital}$ is due to the magnetic moment of electrons in orbital, the field associated with $B_{Lattice}$ is classical dipolar field which is contributed by neighboring atomic site and where B_{Fermi} is the Fermi contact term. The interaction of orbital moment $\vec{l}$ and nuclear spin $\vec{I}$ located at site $\vec{r} = 0$ with electron spin $\vec{s}$ is given by

$$B_{FF}^{tot} = 2\mu_B\gamma_\rho\hbar\vec{l}\left[\frac{\vec{l}}{r^3} - \frac{\vec{s}}{r^3} + 3\frac{(\vec{r}\cdot\vec{s})\vec{r}}{r^5} + \frac{8}{3}\pi\vec{s}\delta(\vec{r})\right] \quad 2.9$$

where, the first term in above equation exhibits the magnetic field of orbital moment, the second and third show the magnetic moment of electron spin and the last term is the Fermi contact interaction.

The Fermi contact term can be calculated by using the electronic spin density up ($n_s^\uparrow$) and down ($n_s^\downarrow$) of electrons at probe sites ($n_s(0)$)

$$B_{Fermi} = \frac{8\pi}{3} \mu_B [n_s^\uparrow - n_s^\downarrow] \quad 2.10$$

To add the relativistic correction term, the spin density has to be averaged over the Thomson radius [98].

$$r_T = \frac{Ze^2}{mc^2} \quad 2.11$$

The contact hyperfine fields further splits into two components core and valence hyperfine. It is very difficult to determine the core and valence hyperfine field experimentally, while on other hand the calculation of both are very straight forward computationally [98-102].

The nuclear magnetic moment $\vec{\mu}_I$ is

$$\vec{\mu}_I = \gamma \hbar \vec{I} \quad 2.12$$

In the presence of the external magnetic field $\vec{B}_{ext}$ the interaction energy is,

$$W_{ext} = -\vec{\mu}_I \cdot \vec{B}_{ext} \quad 2.13$$

The calculated values of EFG at atomic sites are useful for experimentalist to measure the electric quadrupole moment of particular atom which is a nuclear parameter and have numerous applications in nuclear physics.

Chapter 3

COMPUTATIONAL DETAILS

3.1 Many Body System

Unit cell is the basic building block of a material which provides various information about the crystalline solids. All materials are built by the arrangement of small repetitive unit cell and unit cell consists of atoms [103]. Quantum mechanically the unit cell contains two types of particles, electrons N and nuclei N_0 . These two interact among themselves as well as with each other by number of ways [104]. Information about a system can be derived from the solution of Schrödinger wave equation for each electron and nucleus of the system. The system has the wavefunction in the following form

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots \dots \dots \vec{r}_N; \vec{R}_1, \vec{R}_2, \vec{R}_3, \dots \dots \dots \vec{R}_N) \quad 3.1$$

where $\vec{r}$, and $\vec{R}$ show the positions of electrons and nuclei respectively. The Schrödinger wave equation in Bra-ket notation for such a many body system becomes;

$$\hat{H}|\Psi_i(r, R)\rangle = E|\Psi_i(r, R)\rangle \quad 3.2$$

this is the Eigen value equation for a system where $\hat{H}$, $|\Psi_i(r, R)\rangle$ and E show Hamiltonian operator, Eigen function and Eigen energy values respectively. The Hamiltonian operator is the sum of number of interaction energy which can be written as,

$$\hat{H} = \hat{U}_{cc} + \hat{U}_{ee} + \hat{U}_{ce} + \hat{T}_c + \hat{T}_e \quad 3.3$$

where

- (i) $\hat{U}_{cc}$: shows the interaction energy between two nuclei.
- (ii) $\hat{U}_{ee}$: stands for interaction energy between two electrons.
- (iii) $\hat{U}_{ce}$: exhibits the interaction energy between electron and nuclei.
- (iv) $\hat{T}_c$: stands for kinetic energy of nuclei.
- (v) $\hat{T}_e$: shows the kinetic energy of electrons.

All these quantum energy operators are defined in terms of atomic unit system as;

$$\hat{U}_{cc} = \sum \frac{ZZ'}{R - R'} \quad 3.4$$

$$\hat{U}_{ee} = \sum \frac{1}{r_i - r_j} \quad 3.5$$

$$\hat{U}_{ce} = - \sum \frac{Z}{r_i - R} \quad 3.6$$

$$\hat{T}_c = \sum_1^{N_0} \frac{1}{2} \nabla_{R_i}^2 \quad 3.7$$

$$\hat{T}_e = \sum_{i=1}^N \frac{1}{2} \nabla_{r_i}^2 \quad 3.8$$

where r_i and R show position of electrons and nucleus and Z shows charge of the nucleus. Analytically the solution of these equations are very difficult, therefore certain approximations are used to simplify the differential equation. The mass of a nucleus is very large compared to mass of electron therefore, the kinetic energy operator term of nucleus will be ignored. This was suggested by Born-Oppenheimer and is called Born-Oppenheimer approximation [105]. The new Hamiltonian is called Born-Oppenheimer Hamiltonian i.e,

$$\hat{H}(BO) = \hat{U}_{cc} + \hat{U}_{ee} + \hat{U}_{ce} + \hat{T}_e \quad 3.9$$

similarly, Schrödinger wave equation becomes after Born-Oppenheimer approximation

$$\hat{H}(BO)|\Psi\rangle = E(BO)|\Psi\rangle \quad 3.10$$

But the electronic energy can be written in form of Hamiltonian which is defined as,

$$\hat{H}_{elec} = \hat{U}_{ee} + \hat{U}_{ce} + \hat{T}_e \quad 3.11$$

The electronic ground state properties can be derived from the following equation

$$\hat{H}_{elec}|\Psi(r, R)\rangle = E_{elec}|\Psi(r, R)\rangle \quad 3.12$$

equation (3.12) stands for a single electron, if we have avagadro number of electrons or atoms then the avagadro number of equation which is very difficult task to solve. An alternative method is needed to solve this complexity; common alternative approach to treat the problem properly is density functional theory [DFT]. DFT does not treat individual particle wave function. It takes the ground state electrons density $n_0(r)$ as a basic single variable instead of wave functions of each electron. Density functional theory has the potential to solve the problem of many body wavefunction by considering the issue with the electronic density $n = n(r)$ of the system. The electronic density is a function of position only. Kohn and Sham modified the ground state functional of Hohenberg and Sham i.e.,

$$E[n(r)] = \frac{1}{2} \int d^3r' d^3r \frac{n(r)n(r')}{|r-r'|} + \sum \langle \Psi | (-\frac{\nabla^2}{2}) | \Psi \rangle + \int d^3r V_{ext}(r)n(r) + E_{xc}(n) \quad 3.13$$

in equation (3.13) each term can be explained as;

- (i) $\frac{1}{2} \int d^3r' d^3r \frac{n(r)n(r')}{|r-r'|}$ - this term shows the repulsion of the electronic density

which is also called Hartree energy.

- (ii) $\sum \langle \Psi | (-\frac{\nabla^2}{2}) | \Psi \rangle$ - shows kinetic energy of electrons.
- (iii) $\int d^3r V_{ext}(r)n(r)$ – stands for electrons nuclei interaction energy.
- (iv) $E_{xc}(n)$ – this last term exhibits the exchange-correlation term, which is necessary to balance the energy of the system to the exact ground state energy of the considered system.

The exact calculation of exchange correlation term is very difficult. There is no known method to calculate exchange correlation effect, however number of approximations are used to calculate ground state parameter with appropriate accuracy. The most common and versatile approximations for calculation of exchange correlation effect are local density approximation (LDA), generalized gradient approximation (GGA) with different potential, LDA with Hubbard U (LDA+U) and GGA plus Hubbard U (GGA+U) as well as hybrid functional HF- with different flavors like HF-PBESol, HF-WC and HF-B3PW91. All these approximations are discussed below in details.

3.2 Local Density Approximation

LDA is the most common and basic approximation used in condensed mater physics. Kohn and Sham considered many body system as homogenous gas with uniform density $n_0(r)$. The exchange-correlation energy E_{xc} is a functional of uniform electron density, which is;

$$E_{xc}^{LDA}[n(r)] = \int n(r) E_{xc}^{hom} n(r) dr \quad 3.14$$

The E_{xc} further split into two parts i.e, E_x^{hom} and E_c^{hom} which are the exchange and correlated term respectively;

$$E_{xc}^{homo} = E_x^{hom} + E_c^{hom} \quad 3.15$$

The exchange part can be calculated by using Hartree-Fock methods which is;

$$E_x^{hom} = - \left[\frac{3}{4} \left(\frac{3}{\pi} \right)^{5/3} \right] \int n^{4/3}(r) dr \quad 3.16$$

while the correlation part E_c^{hom} is obtained by subtraction of exchange part from known total energy E_{xc}^{homo} . The LDA has some limitations. Its calculated lattice constant underestimates and cannot treat strong electronic system [106]. LDA is improved by taking spin into account in form of local spin density approximation LSDA which treat magnetic system with large accuracy but for heavy electron system it faces some limitation. LDA and LSDA results can be improved if we consider realistic approach that density of particle is not uniform.

3.3 Generalized Gradient Approximation

The LDA is a common primary tool and yields appreciable results in some cases. LDA treats electron density uniformly inside the material but the real picture is very different. The density of electron in an atom is not uniform, but it is a function with respect to nucleus position inside the atom. The generalized gradient approximation GGA was introduced [107]. In GGA energy is a functional of both electron density $n_0(r)$ and its gradient $\nabla n_0(r)$. It means the system as a whole is non-homogenous. The GGA exchange-correlation functional E_{xc}^{GGA} is defined as:

$$E_{xc}^{GGA} = \int f_{xc}^{GGA}(n_0(r)) \nabla n_0(r) d\tau \quad 3.17$$

where, f_{xc}^{GGA} shows exchange correlation energy which is a function of electron density.

As the electrons have intrinsic spin property so equation (3.17) becomes

$$E_{xc}^{GGA}[n_0(\mathbf{r}, \uparrow\downarrow)] = \int f_{xc}^{GGA}(n_0(\uparrow\downarrow)) \nabla n_0(\mathbf{r}, \uparrow\downarrow) d\tau \quad 3.18$$

GGA gives better results for number of materials as compared to LDA. The most commonly used GGA potentials are;

- (i) Perdew-Burke-Ernzerhof exchange correlation functional “PBEsol-96” [107-108].
- (ii) Perdew and Wang correlation functional “PW-91” [109].
- (iii) Lee-Yang-Parr's correlation functional “LYP-88” [110].
- (iv) Axel-Becke exchange functional “B-88” [111].
- (v) Perdew’s correlation functional “PW-86” [112-113].
- (vi) Wu-Cohen density gradient functional “Wu-C” [114].
- (vii) Engel-Vosko correlation functional “E-V” [115].

3.4 Generalized Gradient Approximation with Hubbard U

LDA and GGA are good approximations to explain the structural properties of number of p- orbital elements and its corresponding compounds. But in case of transition, lanthanides and actinides elements d- and f- state orbital such potentials are insufficient to explain the structural, electronic and magnetic properties. This error arises from the self-interaction error in LDA and GGA. In order to solve the issue the LDA and GGA approximations need to be modified. An efficient method used to overcome the self interaction error in LDA and GGA approximation mainly for highly correlated d- and f- states. Both LDA and GGA XC- functional do not treat well the valence electrons in number of cases; a well known controversial example is Mott insulator which predicted by LDA and GGA as metallic. The DFT+U approaches are introduced based on Hubbard model Hamiltonian. The DFT+U [116-117] technique is the modified simple approach with low computational cost. Hence, an additional correction term which is known as

Hubbard (U) is added to LDA and GGA which convert these to LDA+U and GGA(PW-86)+U, GGA(PW-91)+U, GGA(PBEsol)+U, GGA(E-V)+U etc. The basic expression for GGA plus Hubbard (U) is [116-119]:

$$E^{GGA+U} = E_{GGA} + E_U \quad 3.19$$

$$E^{GGA+U} = E_{GGA} + \frac{(U-J)}{2} \left(N \sum_{m,\sigma} n^2(m, \sigma) \right) \quad 3.20$$

where, (i) U shows Coulomb interaction term (ii) J stands for Exchange interaction (iii) N is the total number of electrons (iv) n, m, σ , where n is the occupation number of orbital m with spin σ and $U - J$ is called effective potential ($U_{effective} = U - J$).

3.5 Onsite-Exact-Exchange and Hybrid Functional for Correlated Electrons

Besides standard LDA and GGA, the Hartree-Fock (HF) with different flavors are also appreciable for strongly correlated electron system. The hybrid Hartree-Fock or onsite-exact exchange method applies to a single orbital of an atom. The Hartree-Fock have the common mathematical form which was suggested by Moreira *et al* is:

$$E_{xc}^{onsite-HF}[\rho] = \alpha(E_x^{HF}[\Psi_{core}] - E_x^{SL}[\rho_{core}]) + E_{xc}^{SL}[\rho] \quad 3.21$$

where, α is the Hartree-Fock exchange fraction (between 0 and 1) and E_{xc}^{SL} is the semi local (SL) functional [120]. The onsite exact exchange functional has following approximation

- (i) PBE: XC_PBE with indxc=13.
- (ii) LDA:XC_LDA with indxc=5.
- (iii) PBEsol:XC_PBEsol with indxc=19.
- (iv) WC:XC_WC with indxc=11.

(v) B3PW91:XC_B3PW91 with indx=18. [110-111,120-125].

3.6 Spin-Orbit Coupling

The interaction of orbital and spin angular momentum or magnetic moment of particle is called spin orbit interaction or spin orbit coupling in quantum mechanics. The SOC effect cause splitting of energy levels of an atom or molecule. The most common example is the shifting of electronic energy level due to the electromagnetic interaction between orbital and spin magnetic field generated by electron cloud around the nucleus. The SOC effect varies from atom to atom. The SOC phenomenon is relativistic in nature and it is dominant especially in those atoms where the v^2/c^2 (where v is the speed of particle and c is the speed of light) change rapidly. This rapid variation is dominant in heavy fermions, like uranium, neptunium, plutonium etc., due to the large nuclear charge and large orbitals of an atom. In heavier atoms the spin orbit interaction is large than spin-spin and orbit-orbit interaction due to large size of nuclei and large number of orbitals [126]. The scalar relativistic part of the Schrödinger Hamiltonian is diagonalized in the scalar relativistic basis. After the addition of SOC the new Schrödinger wave equation is:

$$H\Psi = E\Psi + H_{soc}\Psi \quad 3.22$$

where H_{soc} is defined as [127];

$$H_{soc} = \frac{\hbar}{4\pi mc^2} \frac{1}{r} \frac{dV}{dr} \begin{bmatrix} \vec{l} \cdot \vec{\sigma} & 0 \\ 0 & 0 \end{bmatrix} \quad 3.23$$

where $\vec{\sigma}$ is the Pauli spin matrices [128] i.e,

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad 3.24$$

$$S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad 3.25$$

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad 3.26$$

their unitless equivalents Pauli spin matrices are

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad 3.27$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad 3.28$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad 3.29$$

3.7 Full Potential Linearized Augmented Plane Wave plus Local Orbital Method (FP-LAPW) + lo

FP-LAPW + lo is one of the most common and accurate approach to solve Kohn Sham equation for investigation of electronic structure as well as ground state energy of crystal or solid [129]. This approach is based on Augmented Plane Wave (APW) method. On the basis of APW method the space of crystal is divided into two regions, as shown in Fig 3.1:

- (a). Non- overlapping muffin-tin sphere (I)
- (b). Interstitial region (II)

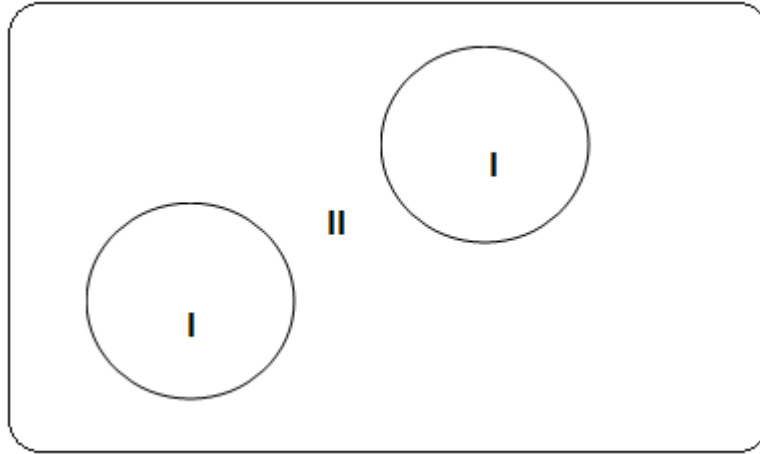


Figure 3.1 Muffin tin spheres (I) with interstitial region (II)

According to APW approach the potential inside the sphere is constant while it varies in interstitial region. The calculated electronic structure and ground state energy is not consistent to experimental result. Hence the actual potential is different from APW approach [130]. The most serious shortcoming of APW method is the treatment of the semi-core states. The valence and the core fermions of heavy atoms are treated semi relativistically as well as fully relativistically. In order to clarify that all the electrons of the system are treated accurately; semi-core states are incorporated and explained with local orbitals. This dilemma was solved by Andersen *et al* and Singh [129-131]. They modified the APW approach by introducing LAPW and FP-LAPW+ lo method. According to LAPW + lo method the potential inside the sphere vary spherical harmonically while the interstitial region potential has a plane wave i.e,

The definition of FP-LAPW basis function is given below:

$$V_{(r)} = \sum_{lm} V_{lm}(r) Y_{lm}(r) \quad (a)$$

$$V_{(r)} = \sum_k V_k e^{ikr} \quad (b)$$

in equation (a) and (b) $V_{(r)}$ is the potential for inside the sphere and interstitial region. For the wave expansion inside the atomic sphere the value of l is confined to l_{max} .

The wave function is expanded in terms of spherical harmonics up to $l_{max}=9$ and for interstitial non spherical part l_{max} is equal to 6. The radii of the MT spheres were chosen for actinide element 2.7 a.u and for post transition metals 2.4 a.u, respectively. These are the well optimized values which stabilized the structure and give fruitful magnetic properties. To provide satisfactory results the Brillouin zone integration is performed on a mesh of $15 \times 15 \times 13$ k-points [132] in the bulk of AcGa_2 , NpX_3 and UX_3 compounds. In present study the expansion of wave

function limited to $l_{max} = 10$, $K_{max} = 9/R_{MT}$ and $G_{max} = 12$. The elected convergence criterion for charge and energy are 0.0001.

3.8 WIEN2k Code and Technical Details

In present work we used WIEN2k code. This code is based on Full Potential Linearized Augmented Plane Wave method plus local orbital. WIEN2k code is used in material science or condensed matter to calculate and predict different structural, electronic, optical and magnetic properties of various materials. WIEN2k is written in FORTRAN90 and developed by Blaha, Schwarz and co-workers [133]. There are Different versions of WIEN with different modifications available (WIEN93, WIEN95, WIEN97, WIEN2k). WIEN2k code works computationally in two parts. In first part the structure file is prepared and passed the structure with initialization process, it treat the Muffin-tin overlapping sphere and generate k-mesh in the Brillouin Zone and detect the symmetry operation. In the second part the self-consistency cycle is performed on the base of Kohn Sham equations to achieve convergences of energy and charge of the material and as an output different properties like optimization of structure, optical as well as magnetic properties, hyperfine field (HFF) and electric field gradient (EFG) etc., are calculated.

Chapter 4

RESULTS AND DISCUSSION

4.1 Theoretical Studies of Actinide Digallides AcGa_2 ($\text{Ac} = \text{U}, \text{Np}, \text{Pu}$)

The quantum chemistry of actinide based molecules is challenging due to their complex electronic structure [3, 134]. One of the interesting families of these challenging compounds is actinides digallide. The different properties like, HFF, EFG, structural, magnetic as well as electronic properties of uranium, neptunium and plutonium based post transition metal gallium have attracted considerable attention in modern condensed matter physics [13, 18, 135, 136]. Actinides 5f electrons system interesting materials due to the exhibition of magnetic and electric hyperfine interaction spin fluctuation, Pauli paramagnetism, heavy fermions and unconventional superconductivity [14-15, 137-138]. The 5f-electron systems like 4f-electron systems [139-143] exhibit dual nature where they can behave as a localized system or as an itinerant system depending on their hosts [10, 48, 144-148].

There are extensive experimental work is reported about the importance of AcGa_2 [$\text{Ac} = \text{U}, \text{Np}, \text{Pu}$] and other related compounds [22, 48, 149-150]. AcGa_2 are intermetallic in nature and exhibit hexagonal AB_2 type crystal structure with space group $\text{P6}/\text{mmm}$. The c/a ratio of AcGa_2 has been increased from U to Pu due to increase of c which is observed by number of experimentalist using X-ray diffraction techniques [18, 20, 135, 151]. Yaar *et al.* [13] Honma *et al.* [18] and Honma *et al.* [18] investigated the ferromagnetic nature NpGa_2 and UGa_2 with curie temperatures of 55K and 125 K, respectively using AC, DC and Mössbauer techniques and found to be 5f localized systems. The X-ray diffraction study indicated that there is a

considerable orthorhombic distortion of UGa_2 occurs below 100 K [11, 152]. The neutron diffraction study shows that uranium has magnetic moment $3.0\mu_B/\text{U}$ while the magnetization study exhibits $2.7\mu_B/\text{U}$ in uranium digallide [12, 153]. The experimentally investigated magnetic moment of NpGa_2 is $2.3 \mu_B/\text{Np}$ [13]. The PuGa_2 is an antiferromagnetic material. The antiferromagnetic nature of PuGa_2 has been studied by Boulet *et al.* [20] using specific heat and magnetic susceptibility experimental technique and concluded the Néel temperature of 74 K. The effective magnetic moment of Pu is measured experimentally by Boulet *et al.* to be $0.42 \mu_B$, which is much smaller than that of the Pu^{3+} free ion ($2.6 \mu_B$) [20].

Electric field gradients for these materials have been investigated for the first time. To understand the magnetic properties of an atom the distribution of electronic charge around the atomic site is very necessary [154-155]. EFG is one of the most powerful computational tools for investigation of environmental study of atomic site [156-159]. The non spherical structure of quadrupole nuclei ($I > \frac{1}{2}$) has non anisotropic charge density inside the nucleus and has both positive and negative electric quadrupole moment. The non-zero electric field gradient and nuclear electric quadrupole moment interact to each other. The strength of such interaction helps to explore the shape of orbital, bonding nature, deviation of electrons from spherical symmetry, vacancies and impurities, quadrupole frequency and splitting of energy levels [160-164].

To the best of our knowledge no computational studies of intermetallic actinide digallide AcGa_2 system are present in literature due to its heavy fermions, Pauli paramagnetism and spin fluctuation nature. In present work, we investigate number of properties like, structural, EFG, magnetic structure as well as magnetic moment and HFF of AcGa_2 by using various computational functionals, like local density approximation (LDA) in absence and addition of Hubbard potential (LDA+U), generalize gradient approximation with Hubbard U and special

hybrid functional B3LYP. All the present compounds AcGa_2 are heavy fermions in nature. These compounds have 4f- and 5f- electrons, so spin orbit coupling effect should be effective. We also used spin orbit coupling calculation for getting fruitful results.

4.1.1 Structural Properties of AcGa_2 ($\text{Ac} = \text{U}, \text{Np}, \text{Pu}$)

AcGa_2 [$\text{Ac}=\text{U}, \text{Np}, \text{Pu}$] compounds show most common AB_2 type hexagonal crystal geometry with space group $\text{P6}/\text{mmm-D}$ (191). The atomic position of actinide ($\text{Ac}=\text{U}, \text{Np}, \text{Pu}$) are 1(a); (0.0, 0.0, 0.0) while gallium has 2(d) (1/3, 2/3, 1/2) ; (2/3, 1/3, 1/2) [48, 165-166]. The experimental lattice constant and angle of actinide digallide are ($a=4.210 \text{ \AA}$, $b=4.210 \text{ \AA}$, $c=4.010 \text{ \AA}$ and $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ UGa_2), ($a=4.2590 \text{ \AA}$, $b=4.2590 \text{ \AA}$, $c=4.077 \text{ \AA}$ and $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ NpGa_2) and ($a=4.2590 \text{ \AA}$, $b=4.2590 \text{ \AA}$, $c=4.077 \text{ \AA}$ and $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ PuGa_2). The experimental c/a ratio increase from UGa_2 to PuGa_2 . The c/a values of AcGa_2 ($\text{Ac}=\text{U}, \text{Np}, \text{Pu}$) are 0.9530, 0.9570 and 0.9690 [11, 18, 20, 135]. To calculate different properties of AcGa_2 we relaxed the unit cell volume under the consideration of Birch-Murnaghan equation of state. From the optimized state volumes, the structural parameters like ground state energy, lattice constants, bulk moduli and its derivatives are obtained. For optimization of AcGa_2 unit used 2-D optimization package by using different potentials which are shown in Table. 4.1. Both GGA and LDA underestimates the lattice constants 7 to 30% especially for c and 0.5 to 1.4% for a and b as shown in Fig 4.1 (a). In order to improve the results, we used other functional like LDA+U and GGA+U which treat well heavy fermions. The c/a ratio has been calculated computationally. The results of LDA and GGA are far away from the experimental curve while the LDA+U results are well consistent to the experimental which exhibits that LDA+U treat very well the structural properties of f electrons family. As shown in Tab 4.1, the 2D calculations give motivating results which has very small deviation from experimental data and thereby well

optimize the system. It is concluded that computed lattice constants parameters of actinide digallide by LDA+U are satisfy the experimental data. The bulk modulus which exhibits hardness and

strength of a material has been computed for AcGa₂. The bulk moduli are calculated by different exchange potentials as shown in the Table 4.1. The calculated bulk moduli are inversely related to the lattice constant which exhibits that the compressibility is proportional to the lattice constant. The LDA+U confirm this relation as shown in Fig 4.1 (b). The results of other potentials are not consistent inversely. It has been concluded that hardness decreases and compressibility increases when one goes from U to Pu according to LDA+U calculations.

Table 4.1: Comparison of computational and experimental structural parameters like, lattice constants (Å), c/a ratio, bulk moduli (GPa) and their derivative of actinide digallide.

Flavors	Lattice parameter	UGa ₂	±% error	NpGa ₂	±% error	PuGa ₂	±% error
GGA	a=b (Å)	4.1751	0.8	4.2448	1.40	4.2760	0.5
	c (Å)	3.8567	15	3.7678	30.0	3.7971	7.0
	c/a	0.9238	2.0	0.8871	7.00	0.8880	8.0
	B (GPa)	80.978		85.042		88.282	
	B'	1.9111		3.7585		5.4999	
LDA	a=b (Å)	4.1217	8.0	4.1896	6.00	4.2304	0.5
	c (Å)	3.8600	15	3.7468	8.00	3.7609	8.0
	c/a	0.9365	1.5			0.8890	8.0
	B (Gpa)	104.25		112.05		111.71	
	B'	4.2583		8.8189		7.4361	
LDA+U	a=b	4.2290	0.4	4.2590	0.00	4.2600	0.1
	c (Å)	4.0090	0.1	4.0760	0.02	4.1300	0.1
	c/a	0.9470	0.5	0.9570	0.00	0.9690	0.0
	B (Gpa)	137.57		114.58		112.31	
	B'	3.0288		5.2370		5.4530	
GGA+U	a=b	4.2330	0.5	4.2480	0.02	4.3120	4.0
	c (Å)	4.0160	0.6	4.0570	0.40	4.1030	0.1
	c/a	0.9480	0.4	0.9550	0.20	0.9520	1.0
	B (Gpa)	87.158		113.29		119.07	
	B'	3.9321		4.3420		4.7650	
Exp a=b Å		4.21 ^(18,20)		4.26 ^(18,20)		4.25 ^(18,20)	
Exp c Å		4.01 ^(18,20)		4.08 ^(18,20)		4.12 ^(18,20)	
Exp c/a		0.9520		0.9570		0.9690	

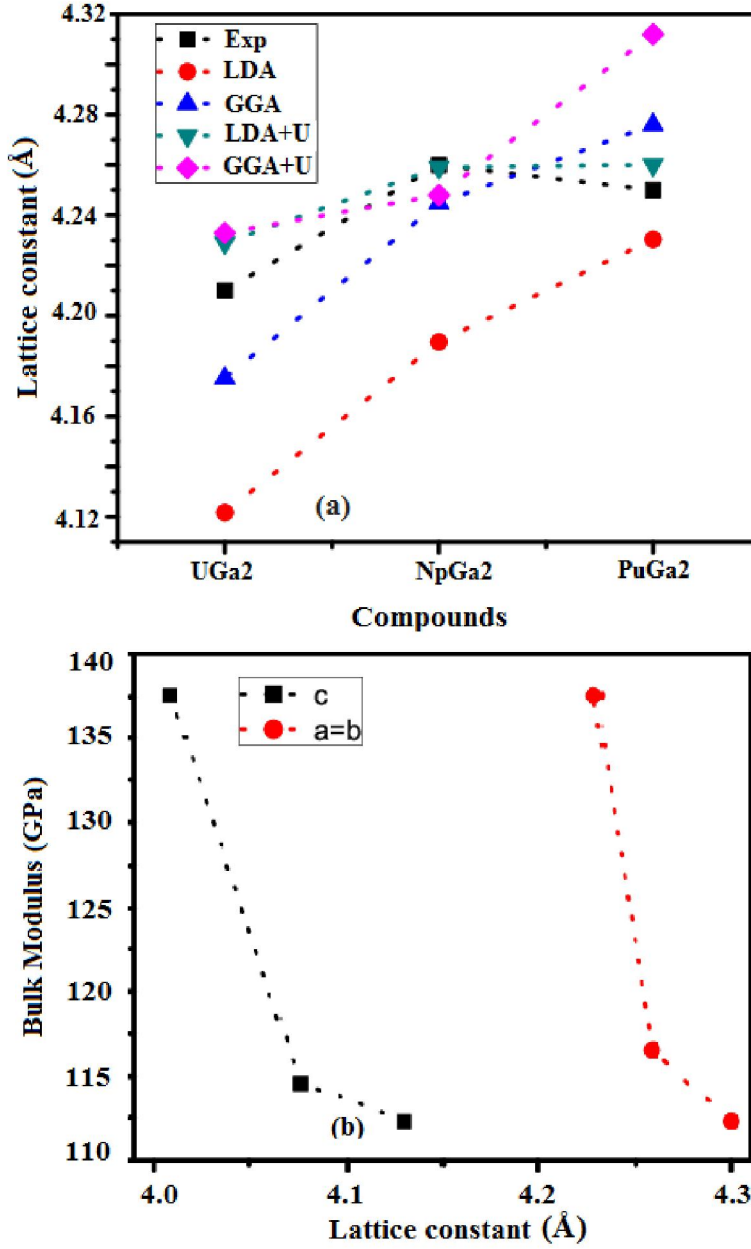


Figure 4. 1: (a) Comparison of calculated and experimental lattice constants of AcGa₂ compounds (b). The bulk modulus versus lattice constant (a=b and c).

4.1.2 Magnetic Properties of AcGa_2 ($\text{Ac} = \text{U}, \text{Np}, \text{Pu}$)

The magnetic behavior of 5f- actinide digallide is very interesting and therefore its detail study is very significant. To explore the magnetic structure of actinide digallides, we relaxed double cell of these compounds by LDA+U. Hence, we find the lowest energies of UGa_2 and NpGa_2 to be -127805.97598684 and -130990.79156800 Ry in the ferromagnetic phase, respectively. The calculated lowest energy of PuGa_2 is -134239.55635983 Ry in anti-ferromagnetic phase as shown in Table 4.2. To inspect the interstitial as well as spin magnetic moments of an atom per unit cell of AcGa_2 , we utilize different functional like, LDA+U and hybrid functional HF-WC. To consider orbital magnetic moments of AcGa_2 , we also include spin-orbit coupling (SOC) to LDA+U and HF. We calculated the spin and interstitial magnetic moment at uranium as well as at gallium sites of AcGa_2 by LDA and GGA. The results are not consistent to the available experimental data. The shortcoming of these two exchange correlation functional are self interaction error. The LDA and GGA are not treating the heavy fermions electrons of d- and f-orbital of an atom. To treat the actinide digallide accurately we try the hybrid functional LDA+U and HF-WC [167] but the outcome still far away from experimental results as shown in Table 4.3. AcGa_2 are heavy fermion so we also used spin orbit coupling calculations. To improve the results the spin orbit coupling calculation are performed. The calculated magnetic moments by LDA+U+SOC and HF-WC+SOC are very near to the experimental results. It means the SOC calculation is appreciable for heavy fermions as shown in Table 4.3 and in Fig 4.2 (a). To calculate the orbital magnetic moment of actinide and gallium atom the SOC calculation is also performed. The magnetic moment of uranium is studied by LDA+U with SOC. The calculated spin, orbital and net magnetic moment of uranium atom are 2.024, -4.374 and 2.35 μ_B/U , respectively which are very close to Lawson *et al.* [12] and Andreev *et al.* results [49]. The

magnetic moment of AcGa_2 is summarized. The dominant contribution in spin magnetic moment of AcGa_2 is due to less than half filled 5f- electron. The calculated magnetic moment at post transition metal Ga is very small in magnitude. The small magnetic moment of gallium exhibits that 3d- shell has no major rule in magnetic moment, while 4p- contributes very small due to less number of fermion in 4p- shell [168]. The orbital magnetic moment of actinide atom has been calculated using spin orbit coupling calculation. The orbital magnetic moment at uranium, neptunium and plutonium atoms are $4.374 \mu_B$, $5.626 \mu_B$ and $4.342 \mu_B$ by using LDA+U+SOC. The orbital magnetic moment increases from uranium to neptunium and then decreases, this due to the different magnetic structure of PuGa_2 . The result of LDA+U+SOC and HF-WC are very appreciable in calculation of magnetic properties of UGa_2 , NpGa_2 and PuGa_2 .

The magnetic moment at uranium and neptunium is due to the 5f- electrons while the s-, p- and d- subshells electrons have small contribution. The spectral notation and ground state term of Np^{+3} ion is 5I_4 , where total angular moment is $J=4$, spin is $S=2$, $L=6$. The effective magnetic moment of neptunium is $m_o = gJ\mu_B = 2.4 \mu_B$, where g is Landé g factor. The magnetic as well electronic properties of neptunium are due to 5f- localized three electrons. The experimental value of total magnetic moment at plutonium site is $0.42 \mu_B$, while theoretical value is $2.6 \mu_B$. Our calculated net magnetic moment of Pu^{+3} is 0.386, which is very close to experimental results. The small magnetic moment of Pu atom indicate the antiferromagnetic nature of PuGa_2 . All the spin, orbital as well as total angular momentum are tabulated in Table 4.3.

To clarify the antiferromagnetic nature of PuGa_2 , we performed double cell calculation for PuGa_2 as shown in Table 4.4. The spin up and spin down magnetic moment at plutonium site completely cancel each other as a result the net magnetic moment at plutonium site is zero which confirm the antiferromagnetic nature of PuGa_2 .

The significant magnetic moments of UGa_2 and NpGa_2 by LDA+U+SO and HF-WC+SO propose that the 5f- electrons are mostly localized at the uranium and neptunium atomic sites, while the less effective moment of PuGa_2 extracted from different potentials propose the delocalization of 5f electron.

Table 4.2: The optimize energy of $2 \times 1 \times 1$ double cell of actinide digallide AcGa_2 .

Compounds	AFM(Ry)	FM(Ry)	Non-Mag(Ry)
UGa₂	-127805.8907245	-127805.9759868	-127805.8806342
NpGa₂	-130990.4886088	-130990.7915680	-130990.4235672
PuGa₂	-134239.5563598	-134239.1301245	-134239.3124523

Table 4.3: Calculated spin magnetic moments inside the MT spheres, orbital and interstitial magnetic moment in the unit cell of AcGa_2 by LDA+U and HF-WC with and without of SOC in the unit of bohar magneton (μ_B).

Compounds	Sites	Magnetic moment							
		LDA+U Spin(μ_B)	HF- WC Spin(μ_B)	LDA+U (SOC) Spin(μ_B)	μ_{Orb}	$ \mu_{\text{tot}} $	HF- WC +(SOC) Spin(μ_B)	μ_{Orb}	$ \mu_{\text{tot}} $
UGa₂	M ^{int}	0.269	0.435	0.274	-----	0.274	0.244	-----	0.244
	M ^U	2.117	2.045	2.024	-4.374	-2.35	1.641	-4.296	2.65
	M ^{Ga}	-0.013	0.031	-0.013	-0.009	-0.02	-0.009	-0.007	0.02
	M ^{tot}	2.373	2.511			-2.09			2.42
Exp	3.0/U ^[49]								
	2.7/U ^[12]								
NpGa₂	M ^{int}	0.915	0.231	0.350	-----	0.350	0.2167	-----	0.217
	M ^{Np}	4.115	3.831	3.019	-5.624	-2.61	3.029	-5.316	2.29
	M ^{Ga}	0.019	0.032	-0.007	-0.004	-0.01	-0.017	-0.008	0.03
	M ^{tot}	5.049	4.094			-2.27			2.09
Exp	2.39/Np ^[13]								
	2.6/NpGa ₂ ^[13]								
PuGa₂	M ^{int}	0.686	0.325	0.447	-----	0.447	0.213	-----	0.213
	M ^{Pu}	5.057	4.923	4.728	-4.342	0.386	4.449	-4.279	0.17
	M ^{Ga}	-0.047	-0.021	-0.017	-0.007	-0.03	-0.023	-0.006	0.02
	M ^{tot}	5.696	5.227			0.839			0.35
Exp	0.42 ^[20]								

Table 4.4: The net magnetic moment of Pu and Ga in double cell of PuGa_2

Sites	LDA	HF-WC
M ^{Int}	0.0000	0.0000
Pu ^{dn}	0.0057	-0.0018
Pu ^{up}	-0.0057	0.0018
Ga	0.0000	0.0000
M ^{total}	0.0000	0.0000

4.1.3 Hyperfine Field of AcGa₂ (Ac = U, Np, Pu)

The nuclear and electronic magnetic field interacts to each other as a result magnetic hyperfine field arises around the atomic sites in the crystal or compounds. The EFG and total hyperfine field interaction give information about the environment around the nuclear site. Such type of interaction can be calculated by numerous experimental techniques like, NMR, Mössbauer spectroscopy and PAC method. The total HFF consists on Fermi contact, dipolar and orbital hyperfine field. The Fermi contact (FC) field is the sum of core and valence hyperfine field. Fermi contact part of hyperfine field (HFF_{FC}) can be computed by downward and upward spin DOS [$n_s^{\uparrow\downarrow}$] at the nuclear sites using Pauli approximation inside the non-relativistic limit

$$HFF_{FC} = \frac{8\pi}{3} \mu_B^2 [\rho_s^{\uparrow}(0) - \rho_s^{\downarrow}(0)] . \quad 4.1$$

The relativistic correction can be computed by taking average spin density and Thomson radius $r_T = Ze^2/mc^2$. In this work, special concentration are devoted to the question that cannot be directly answered by the experiment. The question is that which contributions, *i.e.*, Fermi, dipolar or orbital, are dominant in the magnetic HFF and what is the source of a non-zero HFF at the U, Np and Pu as well as Ga atomic sites. To compute HFF we utilized FP-LAPW scheme as embedded in WIEN2k. The resultant (HFF) is calculated by the following formula [15, 85, 169-172] including core (H_{hf}^c), valence (H_{hf}^v), orbital (H_{hf}^{orb}) and dipolar (H_{hf}^{dip}) contributions:

$$H_{hf}^{tot} = H_{hf}^c + H_{hf}^v + H_{hf}^{orb} + H_{hf}^{dip} . \quad 4.2$$

Our evaluated net as well as orbital, Fermi contact and dipolar HFFs are tabulated in form of Table 4.5. For each atom of the AcGa₂ compound within LDA, GGA, HF-WC and LDA+U. The Fermi contact field has small magnitude due to the opposite sign of valence and

core HFF of electrons. The valence hyperfine originate due to the hybridization of local f- state electrons and neighboring p- and d- state of adjacent atoms, while the core hyperfine field arises due to the interaction of inner s- and p- states electrons. Hence, it is accomplished that Fermi contact HFF is calculated from the contribution of local and adjacent atomic magnetic moments.

The valence contribution in HFF is less in contact field than core in uranium, neptunium and plutonium and majority of inner electrons magnetic moments are parallel to each other while minor are antiparallel. The orbital HFF is very large in magnitude as shown in the Table 4.5 and Fig. 4. 2. (b, c, d). The dominant contribution is owing to p- and f- electrons. There is an increasing trend in orbital magnetic moment at actinide site, due to the varying of electrons in f- states. It is recommended that the source of the dipolar orbital and contribution of the HFF is exchange interaction of p-and f- state electrons in uranium, neptunium and plutonium sites, while p- and d- orbital contributed in gallium. The total HFF also increases from uranium to plutonium an AcGa_2 series as shown in Table 4.5.

The dipolar magnetic moment which is due to spin of electron has been calculated as shown in Table. 4.5 and Fig. 4.2 (b, c, d). As the s- and p- orbital of actinide atom are filled, the dipolar HFF for these are negligible while the major donation arises due to d- and f-orbital, while p-orbital contribution is dominant in gallium.

The increase in HFF has been computed in AcGa_2 , when one move from UGa_2 to PuGa_2 by using different exchange correlations likes HF-WC and LDA+U. The systematic increase of HFF at actinides site is due to the varying spin magnetic moment as well as different atomic number. The comparison of HFF at actinide sites by different functionals have been tabulated in the form of Table. 4.5. The larger value of Pu is due to the delocalized 5f electrons. The valence electrons in U and Np atoms are localized in contrast to Pu atom. At the Ac site of AcGa_2

compounds, the HFF is larger for Ac = Pu than those for Ac = U and Np due to the larger number of f-electrons in Pu atom than those in U and Np atoms.

The gradual increase of the core HFF from UGa_2 to PuGa_2 at actinide site is interrelated to the local moment of actinide site. It is computed that core HFF direct related to the local moment, means the raise of local moment cause increase of core HFF. The interpretation of such behavior is the interaction of polarized electrons to the neighboring s- and p- fermions. A similar trend has been observed in gallium atom. The calculated local moment of gallium atom is very small in AcGa_2 ; hence the dipolar and core contribution in AcGa_2 is tiny. The HFF at gallium site in PuGa_2 is larger than UGa_2 and NpGa_2 due to dominant hybridization of gallium valence shell electrons to 5f- electrons of plutonium atom. The large value of Fermi contact (HFF) at Uranium, Neptunium and Plutonium site can be qualitatively clarified as follows. The minority s- electrons of the core of actinide repealed from the d- and f- shell electrons while majority electrons full by polarized d- and f- state as a result exchange interaction is attractive [171]. The ratio of HFF to atomic magnetic moment [$C=\text{HFF}/\mu_B$] of actinide atom is going to increase from U to Pu. The variation in C value is due to the varying 5f- electrons. The negative C value exhibits the anti alignment of core polarization and atomic magnetic moment, while positive shows the core polarization align to magnetic moment [102]. These are the suggested HFF values of actinide digallide series for experimentalists to measure magnetic hyperfine interaction energy at uranium, neptunium and plutonium as well as gallium sites.

Table 4.5: Calculated Fermi, Orbital and Dipolar contributions to the (HFF) at the U, Np, Pu and Ga atoms in AcGa_2 compounds by different exchange functional, LDA, GGA, HF- WC and LDA+U in presence of SOC.

Compounds	HFF (KGAUSS)	LDA	GGA	HF-WC	LDA+U
UGa_2 -	$ H_{\text{hf}}^{\text{Tot}} $	-3333.66	-3414.58	-5053.86	-5149.72
UGa_2 -U	$H_{\text{hf}}^{\text{Fer}}$	-335.592	-327.472	-368.891	-391.847
UGa_2 -U	$H_{\text{hf}}^{\text{Orb}}$	-2959.93	-3045.82	-4407.24	-4533.15
UGa_2 -U	$H_{\text{hf}}^{\text{Dip}}$	-38.1293	-41.2880	-277.731	-224.721
UGa_2 -Ga	$ H_{\text{hf}}^{\text{Tot}} $	-63.2850	-72.9223	-106.664	-105.205
UGa_2 -Ga	$H_{\text{hf}}^{\text{Fer}}$	-60.1000	-70.1501	-95.6932	-91.2581
UGa_2 -Ga	$H_{\text{hf}}^{\text{Orb}}$	-2.76600	-2.33982	-8.23800	-9.82100
UGa_2 -Ga	$H_{\text{hf}}^{\text{Dip}}$	-0.41900	-0.43251	-2.73300	-4.12600
NpGa_2 -	$ H_{\text{hf}}^{\text{Tot}} $	-6341.49	-6465.98	-7851.08	-8362.76
NpGa_2 -Np	$H_{\text{hf}}^{\text{Fer}}$	-612.993	-591.042	-613.527	-466.185
NpGa_2 -Np	$H_{\text{hf}}^{\text{Orb}}$	-5725.07	-5874.32	-7153.43	-7724.96
NpGa_2 -Np	$H_{\text{hf}}^{\text{Dip}}$	-3.42210	-0.61610	-84.1213	-171.620
NpGa_2 -Ga	$ H_{\text{hf}}^{\text{Tot}} $	-110.825	-127.136	-122.570	-32.4152
NpGa_2 -Ga	$H_{\text{hf}}^{\text{Fer}}$	-103.464	-120.836	-108.841	-24.6652
NpGa_2 -Ga	$H_{\text{hf}}^{\text{Orb}}$	-5.74013	-5.27421	-10.3732	-4.17100
NpGa_2 -Ga	$H_{\text{hf}}^{\text{Dip}}$	-1.62081	-1.02621	-3.35621	-3.58200
PuGa_2 -	$ H_{\text{hf}}^{\text{Tot}} $	-7970.45	-8222.93	-9760.51	-9764.38
PuGa_2 -Pu	$H_{\text{hf}}^{\text{Fer}}$	-825.341	-791.074	-898.926	-888.007
PuGa_2 -Pu	$H_{\text{hf}}^{\text{Orb}}$	-7181.42	-7460.99	-9021.48	-9065.03
PuGa_2 -Pu	$H_{\text{hf}}^{\text{Dip}}$	36.3152	29.1321	159.890	188.660
PuGa_2 -Ga	$ H_{\text{hf}}^{\text{Tot}} $	-129.246	-154.207	-145.441	-147.032
PuGa_2 -Ga	$H_{\text{hf}}^{\text{Fer}}$	-125.909	-144.699	-136.232	-140.701
PuGa_2 -Ga	$H_{\text{hf}}^{\text{Orb}}$	-5.68620	-5.67431	-8.29321	-9.36321
PuGa_2 -Ga	$H_{\text{hf}}^{\text{Dip}}$	2.34913	-3.83421	-0.91643	3.03214

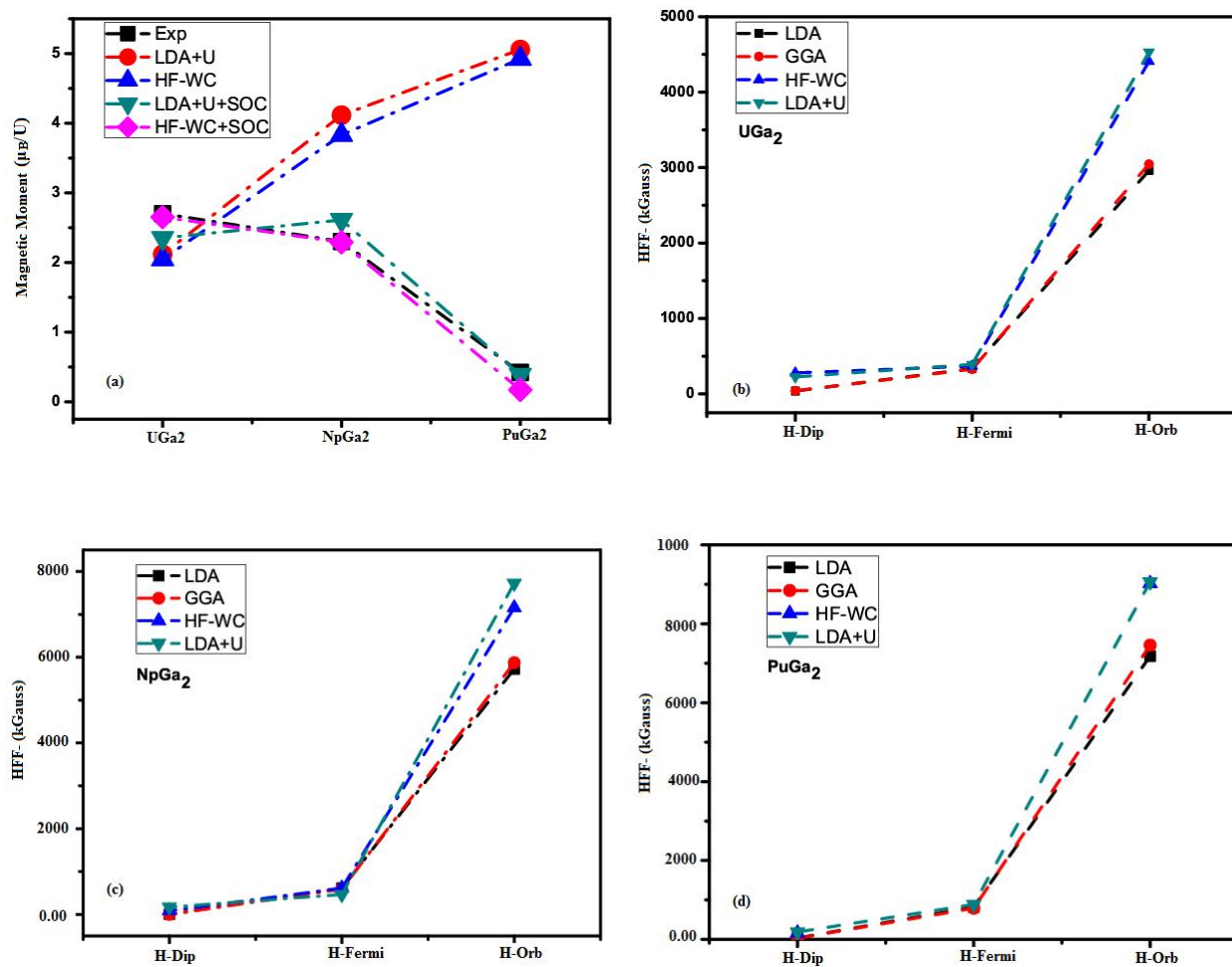


Figure 4.2: (a) Comparison of experimental and calculated magnetic moment of uranium atom in AcGa_2 . (b, c, d) exhibit the dipolar, orbital and Fermi contact HFF at actinide and gallium site.

4.1.4 Electric Field Gradient (EFG) of AcGa₂ (Ac = U, Np, Pu)

EFG is the property of materials, which is the second partial derivative of the electric potential V evaluated at the site of the nucleus. It is traceless second rank symmetric tensor. The Principal component of total EFG (V_{zz}^{total}) can be calculated by the sum of its valence and lattice contributions:

$$V_{zz}^{total} = V_{zz}^{val} + V_{zz}^{latt}, \quad 4.3$$

where valence EFG (V_{zz}^{val}) originates from the non-spherical charge distribution inside the atomic spheres while V_{zz}^{latt} arise due to the interstitial region. The Principle component of the EFG (V_{zz}) can be obtained from L=2 and M=4 component of the potential expansion inside the muffin-tin spheres as follows: [83, 172-173]

$$V_{zz} = \lim_{r \rightarrow 0} \left[\frac{5}{4\pi} \right]^{1/2} \left[\frac{V_{20}(r)}{r^2} \right]. \quad 4.4$$

It is clear from equation (4.4) that the most important component of EFG tensor align to the z-axis, the other important parameter radial electric potential V_{20} , can be calculated as

$$\begin{aligned} V_{20}(r = 0) = & \frac{4\pi}{5} \int_0^{R_{MT}} \frac{\rho_{20}}{r} dr - \frac{4\pi}{5} \int_0^{R_{MT}} \frac{\rho_{20}}{r} \left(\frac{r}{R_{MT}} \right)^5 dr \\ & + 4\pi \sum_k V(k) J_2(kR_{MT}) Y_{20}(\hat{k}), \end{aligned} \quad 4.5$$

where equation (4.9) consist of valence and lattice EFG. The first term of the equation (4.9) is contributed by the valence electrons of the atomic sphere while the other terms exhibit the contribution of lattice part of the atomic sphere. As the atomic sphere have three dimensional geometry, so $J_2(kR_{MT})$ specify Bessel function in spherical coordinates with radius R_M and the

other term ρ_{20} shows density of expansion with $L=2$ and $M=0$. The value of EFG of a single atom varies from materials to material. It means that the EFG for a specific atom can be small or zero in one compound, while it can be non-zero and large in another compound. It means it behave like a fingerprint in materials [174-175]. Theoretically, knowledge of the EFG's at the atomic sites suffices to predict the U, Np and Pu nuclear quadrupole coupling constant (Cq) as well as Mössbauer quadrupole splitting Δ in the compound [176]. The quadrupole splitting is given by

$$\Delta = \left| \frac{e^2 q Q}{2} \right| \sqrt{1 + \frac{\eta^2}{3}}. \quad 4.6$$

where η , eq, Q and e show asymmetry parameter, the principal component V_{zz} of EFG tensor, nuclear quadrupole moment and electronic charge [177]. The valence, lattice as well as partial EFG of AcGa_2 have been computed for the first time by using different exchange correlation functionals. Owing to some limitations of LDA and GGA as discussed previously we mention here only the results of LDA+U and GGA+U. The calculated total, lattice and valence contributions as well as different characters of EFG at both Ac and Ga sites in AcGa_2 within various functional are tabulated in Table 4.6. According to our calculated data the total EFG (V_{zz}^{tot}) at Ac site decreases from U to Pu within all considered approaches. The EFG has positive as well as negative values. The negative EFG exhibit the oblate type charge distribution while positive EFG show prolate. In present study the EFG of uranium, neptunium and plutonium is positive. The positive EFG show that these entire atoms have prolate type geometry. The EFG of different energy sub shells have been calculated for the first time in AcGa_2 compounds. The gallium atom has negative EFG in UGa_2 and NpGa_2 , which means oblate type geometry, while gallium also exhibit prolate type environment. It is observed that p-f and s-d contribution in valence EFG is very small as compared to f-f, d-d and p-p orbital. As shown in Table 4.6, the

major contribution arises due to the f-f (5f), d-d (3d) and p-p (4p) orbital. The non-zero EFG of sub energy level confirm the aspherical electronic distribution in orbitals. The gallium has small EFG as compared to uranium, neptunium and plutonium due to the closed 3d- orbital. The small value arises due to the extension of neighboring atomic wavefunction of other atom. The leading rule of EFG in UGa₂ is due the f-f and p-p character which exhibit the non spherical symmetry of these orbitals. The large value of f-f and p-p show that quadrupole coupling constant of these compound is due to its non-spherical distribution of electrons. The GGA+SOC and LDA+SOC calculation shows that the major contribution to total EFG is due to the p-p orbitals. The values of p- orbitals are 20.009 V/m² and 20.156 V/m². The net EFG of neptunium is positive which predicts the prolate shape geometry. The valence and lattice EFGs of Pu atom in plutonium digallide are 4.3185×10^{21} V/m², 4.363×10^{21} V/m² and -0.2163×10^{21} V/m² and -0.2125×10^{21} V/m² by LDA+SOC and GGA+SOC. All the p-, d-, and f-orbitals of Pu are non-spherical in nature, as tabulated in Table 4.6. However, the large EFG at Ga site in PuGa₂, 0.8838 and 0.6213×10^{21} V/m², mainly originates from the non-spherical p-orbital so that contributions of the d- and f-orbitals can be almost neglected.

The EFG increases when we use LDA+SOC and GGA+SOC instead of LDA and GGA, as shown in Figure 4.3, which is consistent to other results. The nuclear quadruple coupling constant (C_q) is an essential parameter used for the investigation of Mössbauer quadrupole splitting in atom as well as in a material. The nuclear electric quadrupole moment (Q) of U, Np, Pu and Ga are 4.936 barn, 3.866 barn, -2.3191 barn and 0.105 barn, respectively [178-179]. The nuclear electric quadrupole coupling constants ($C_q = eV_{zz}Q/h$) of actinide digallide (AcGa₂) have been computed for the first time for Ac (U, Np, Pu) and Ga atoms which have significant role in NMR and NQR literature. The 5f- and 6p- electrons are deviated from its spherical

symmetry which is the leading contributor in the interaction energy around the uranium, neptunium, plutonium and gallium site. The quadrupole coupling constant of U and Ga in UGa_2 are 128 MHz and 4.00 MHz and 166 MHz and 2 MHz by LDA+SOC and GGA+SOC. The central contribution in (C_q) originate due to the valence non-spherical V_{zz}^{d-d} , V_{zz}^{d-d} and V_{zz}^{f-f} EFGs. The quadrupole interaction energies at U, Np and Pu are due to the result of electric quadrupole moment of nuclei and its consequent valence EFGs of 6p- as well as 5f- electrons, while in case of Ga the interaction is due to the 3d and 4p electrons. The EFG and Q interact to each other due to the quadrupole interaction energy. By the relation, one can easily calculate the quadrupole interaction energy at every site. The quadrupole coupling constant C_q and EFGs increased from uranium to plutonium in AcGa_2 series as shown in Fig. 4.3 (a) and 4.3 (b). The quadrupole interaction energy at different actinide site can easily obtain from $E = hC_q$.

Table 4.6: Calculated EFGs and quadrupole coupling constant at uranium, neptunium and gallium as well as at gallium sites by different exchange-correlation functionals in the unit of 10^{21} V/m^2 with NQCC in MHz.

Compounds	Different functional	V_{zz}^{tot}	$V_{zz}^{\text{p-p}}$	$V_{zz}^{\text{s-d}}$	$V_{zz}^{\text{d-d}}$	$V_{zz}^{\text{p-f}}$	$V_{zz}^{\text{f-f}}$	V_{zz}^{val}	V_{zz}^{lat}	C_q MHz
UGa2-U	LDA	-0.0942	3.5136	-0.1781	-1.7707	0.0085	-1.6730	-0.0997	0.0055	
UGa2-Ga	LDA	-1.6355	-0.7951	0.0277	-0.7258	0.0460	0.0009	-1.4463	-0.1892	
UGa2-U	GGA	0.6131	2.4683	-0.1467	-1.6506	0.0023	-0.0781	0.5952	0.0179	
UGa2-Ga	GGA	-1.4969	-0.6191	0.2973	-0.7606	0.0257	0.0009	-1.0557	-0.4411	
UGa2-U	LDA+SOC	1.0882	-0.2607	-0.0685	-1.8948	-0.0141	3.2949	1.0568	-0.0314	128
UGa2-Ga	LDA+SOC	-1.1692	-0.3194	0.0277	-0.7350	0.0458	0.0007	-0.9802	-0.1890	4.00
UGa2-U	GGA+SOC	1.3950	0.1902	-0.0621	-1.8080	-0.0119	3.4408	1.7490	-0.3540	166
UGa2-Ga	GGA+SOC	-0.9543	-0.0695	0.0298	-0.7577	0.0456	0.0009	-0.7509	-0.2034	2.00
NpGa2-Np	LDA	1.4170	4.2353	0.0703	-1.3045	0.1190	-1.4550	1.6651	-0.2481	
NpGa2-Ga	LDA	-0.5479	0.1429	0.1396	-0.7915	0.0451	0.0009	-0.4630	-0.0849	
NpGa2-Np	GGA	1.8549	3.1603	-0.0370	-1.2609	0.0039	-0.0161	1.8500	0.0048	
NpGa2-Ga	GGA	-0.2328	0.4862	0.0283	-0.7168	0.0449	0.0009	-0.1564	-0.0764	
NpGa2-Np	LDA+SOC	3.3704	10.468	-0.1627	-0.6972	0.0173	-6.2754	3.3500	0.0204	314
NpGa2-Ga	LDA+SOC	-0.3561	0.0597	0.0269	-0.6387	0.0453	0.0008	-0.5060	0.1499	0.80
NpGa2-Np	GGA+SOC	3.3704	10.499	-0.1565	-0.6491	0.0173	-6.2870	3.4237	-0.0533	314
NpGa2-Ga	GGA+SOC	-0.4562	0.2755	0.0287	-0.6267	0.0456	0.0008	-0.2760	0.1802	1.00
PuGa2-Pu	LDA	1.9480	4.1413	0.0344	-1.3456	-0.0002	-0.8886	1.9413	0.0067	
PuGa2-Ga	LDA	1.1224	1.7658	0.0258	-0.5472	0.0453	0.0008	1.2905	-0.1681	
PuGa2-Pu	GGA	1.6831	5.4510	0.0006	-1.9716	0.0049	-2.4374	1.0475	0.6356	
PuGa2-Ga	GGA	1.4232	2.0832	0.4634	-0.5634	0.0452	0.0009	2.0293	-0.6061	
PuGa2-Pu	LDA+SOC	4.1022	20.009	-0.2344	-0.6621	0.0390	-14.833	4.3185	-0.2163	229
PuGa2-Ga	LDA+SOC	0.8838	1.5806	0.0154	-0.5984	0.0451	0.0008	1.0435	-0.1597	4
PuGa2-Pu	GGA+SOC	4.1513	20.156	-0.2376	-0.5512	0.0360	-15.039	4.3638	-0.2125	232
PuGa2-Ga	GGA+SOC	0.6213	1.2990	0.0264	-0.5812	0.0451	0.0008	0.7901	-0.1688	2.00

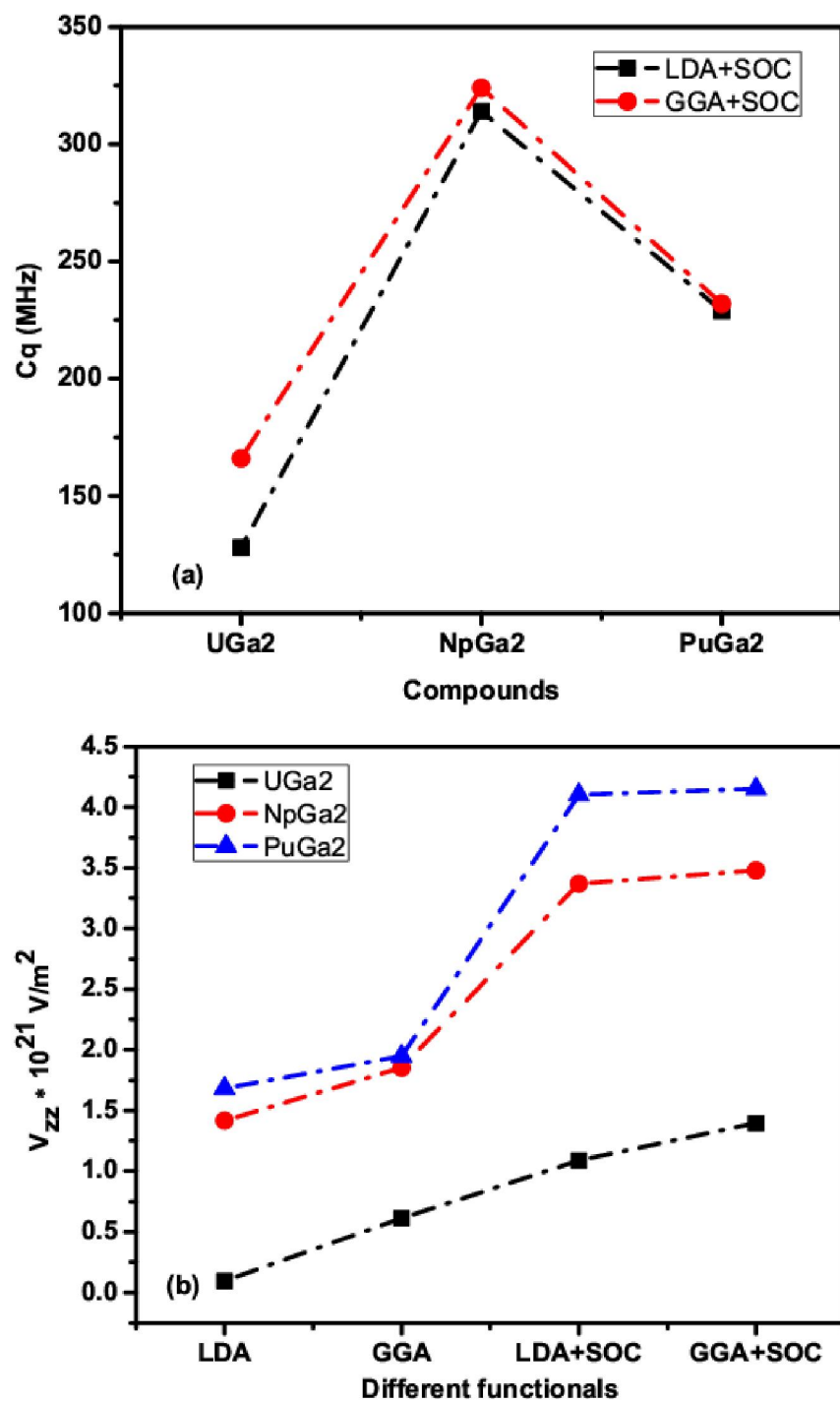


Figure 4.3: (a). Variation of quadrupole coupling constant against different actinide site **(b)**

Principal component of EFG at uranium, neptunium and plutonium site with different functionals.

4.2. Theoretical Studies of NpPx_3 ($\text{Px}=\text{Al, Ga, In}$) Compounds

The actinide NpPx_3 compounds ($\text{Px} = \text{Al, Ga, In}$) crystallize in the AuCu_3 cubic type structure [14, 21, 180-181]. These compounds have 5f electrons. The 5f- electrons exhibits some remarkable and multi properties like, high electronic specific heat, anti-ferromagnetism, unconventional superconductivity, spin fluctuation, paramagnetism, electric and magnetic hyperfine interaction, heavy fermion, ferromagnetism as well Pauli paramagnetism [182-183].

The actinides and their intermetallic compounds have different magnetic properties ranging from local moment behavior (rare-earth like) to itinerant (non localized), band-like character. The broad magnetic nature of actinide is due to the extended wave function of 5f-electron compare to 3d- and 4f- electrons wave function Hill [34] was the former to understand the crucial role of 5f-5f overlapping [184-185]. It may lead to 5f electrons hybridization with neighboring actinide atom as well as strong hybridization with nearest alloying partner s-, p- and d-states. If the An-An separation is smaller than critical value "Hill limit", then 5f electrons strongly delocalize due to direct overlapping such that magnetic order can no longer be supported. At large Np-Np partition, the 5f delocalization is merely probable by the hybridization of 5f electrons with ligand s-, p- and d- orbitals [34]. Sanchez *et al* [186] experimentally studied the magnetic nature of NpPx_3 ($\text{Px}=\text{Al, Ga, In}$) cubic AuCu_3 -type compounds. Colineau *et al* studied NpGa_3 using Mössbauer spectroscopy and powder magnetization resistivity techniques and found antiferromagnetic order at $T_N \approx 65$ K to undergo a first-order transition towards a ferromagnetic state at $T_c \approx 50$ K, while Zwirner *et al.* observed experimentally that NpGa_3 is ferromagnetic under 50 K with magnetic moment $1.6 \mu_B/\text{Np}$ [21, 24, 187]. Gal *et al.* studied by Mössbauer as well as alternating current (AC) and direct current (DC) magnetization techniques and reported that 5f-electrons hybridization plays a

central role in supporting the magnetic properties of NpGa_3 and NpIn_3 . The magnetic moment of neptunium is $1.6 \mu_B$ in NpGa_3 [188]. *Dwight et al.* concluded that NpAl_3 was a ferromagnetic ($T_C = 62.5 \text{ K}$) and a saturation moment of about $1.4 \mu_B$ was determined using Mössbauer measurements, while *Oddou et al* [23] demonstrated that NpAl_3 is actually a type II anti-ferromagnetic ($T_N = 37 \text{ K}$) with a saturation moment of about $1.3 \mu_B$ [189-193]. Large values of electronic specific heat of 100 and $72 \text{ mJmol}^{-1}\text{K}^{-2}$ are due to heavy fermions of neptunium atom have been experimentally measured for NpGa_3 and NpIn_3 , respectively [67, 194-195].

So far, to the best of our information, no serious concentration has been paid to the computational studies of NpPx_3 due to its complex 5f electrons. In this study we explored the structural, magnetic, electronic coefficient of specific heat and electric field gradient (EFG) of these materials in detail with different exchange-correlations functional like local density approximation (LDA), generalized gradient approximation (GGA-PBEsol), Generalized Gradient Approximation (GGA-PBEsol) plus Hubbard potential (GGA+U) and hybrid functional in the presence of spin-orbit coupling.

4.2.1 Structural Properties of NpPx_3 ($\text{Px}=\text{Al, Ga, In}$)

NpPx_3 [$\text{Px}=\text{Al, Ga, In}$] intermetallic compounds exhibit AuCu_3 type cubic crystal structures with space group Pm-3m (221) where Np atom at origin while Px at the face of cube of NpPx_3 . The experimental lattice constants of NpAl_3 , NpGa_3 and NpIn_3 compounds are 4.269, 4.254 and $4.615 \text{ \AA}$ respectively [21, 195-196]. To get the optimized structural properties we relaxed the unit cell volume of NpPx_3 versus total energy and fitted the outcomes with the famous Birch-Murnaghan equation of state [166]. From the stable volumes, the different structural parameters like, lattice constants ($\text{\AA}$), bulk moduli (GPa) and their derivatives, optimized state energy and inter-atomic distances between Np-Np as well as Np-Px are obtained. For optimization of NpPx_3

unit cell we used LDA and GGA (PBEsol) calculation which are implemented in WIEN2k package. The calculated data are tabulated in form of Table 4.7. The ground state lattice constant and unit cell volume are calculated for NpPx_3 by LDA and GGA (PBEsol). The optimized energy versus volume relation is shown in Fig 4.4 (a), (b) and (c). We have obtained that the ground state lattice parameter by GGA is in better agreement with the experimental results compared with LDA as shown in Fig 4.5 (a, b). This is to be expected because the correlation effects is not considered in LDA which leads to the tendency of over binding and smaller lattice constants compared to experimental [195-198].

The bulk moduli are calculated by different exchange potentials as shown in Table 4.7. It is clear from the Fig. 4.5 (b), that GGA (PBEsol) results are in agreement with the experimental results. It is suggested that GGA (PBEsol) calculation treat very well the cubic NpPx_3 structural properties. The Table also shows that NpGa_3 is harder and less compressible as compared to other materials. We have also calculated the pressure derivatives of bulk moduli which is an attractive factor in high pressure physics [199]. The magnetic nature of NpPx_3 has been checked by minimizing unit cell volume versus energy and concluded that these compounds have less energy in ferromagnetic phase which are -118398.14, -138802.03 and -186057.55 Ry for NpAl_3 , NpGa_3 and NpIn_3 respectively. The knowledge of inter-atomic distance between Np-Np and Np-Px is fruitful in understanding the structure and delocalization of electrons in the unit cell. The Np-Np distance is large (3.25 Å) which confirms the delocalization of electrons in NpPx_3 . It has been computed that smaller the bond length between Np-Px greater will be the bulk modulus in NpPx_3 family, as shown in Table 4.7.

Table 4.7: Calculated ground state volume, lattice constant, bulk modulii (GPa), derivative of bulk modulii bond lengths of cubic AuCu₃ type NpPx₃ (Px= Al, Ga, In) in unit cell as well as ground state energies (Ry) for 2×1×1 cell of ferromagnetic and anti-ferromagnetic intermetallic compounds.

	Exp	LDA	GGA- (PBEsol)	Other
NpAl₃				
Volume (Å) ³	77.80	75.00	77.20	
Lattice constant (Å)	4.269 ^[195]	4.212	4.257	
Bulk modulus (GPa)	74.00	94.60	73.32	73±7 ^[195]
B'		5.000	5.000	
E _{FM}			-118398.14	
E _{AFM}			-118398.05	
Np-Np (Å)			4.269	
Np-Al (Å)			3.01864	
NpGa₃				
Volume (Å) ³	76.50	71.40	74.00	
Lattice constant (Å)	4.246 ^[195]	4.149	4.192	
	4.254 ^[196]			
Bulk modulus (GPa)	97 ^[195] 75 ^[21]	104.7	96.30	96±8 ^[195]
B'	6.000 ^[21]	5.000	5.000	
E _{FM}			-138802.03	
E _{AFM}			-138801.94	
Np-Np (Å)			4.246	
Np-Ga (Å)			3.00238	
NpIn₃				
Volume (Å) ³	98.29	91.00	97.30	
Lattice constant (Å)	4.615 ^[195]	4.497	4.550	
Bulk modulus (GPa)	74.00 ^[195]	81.30	73.14	73±2 ^[195]
B'		5.000	5.000	
E _{FM}			-186057.55	
E _{AFM}			-186057.41	
Np-Np (Å)			4.615	
Np- In (Å)			3.263	

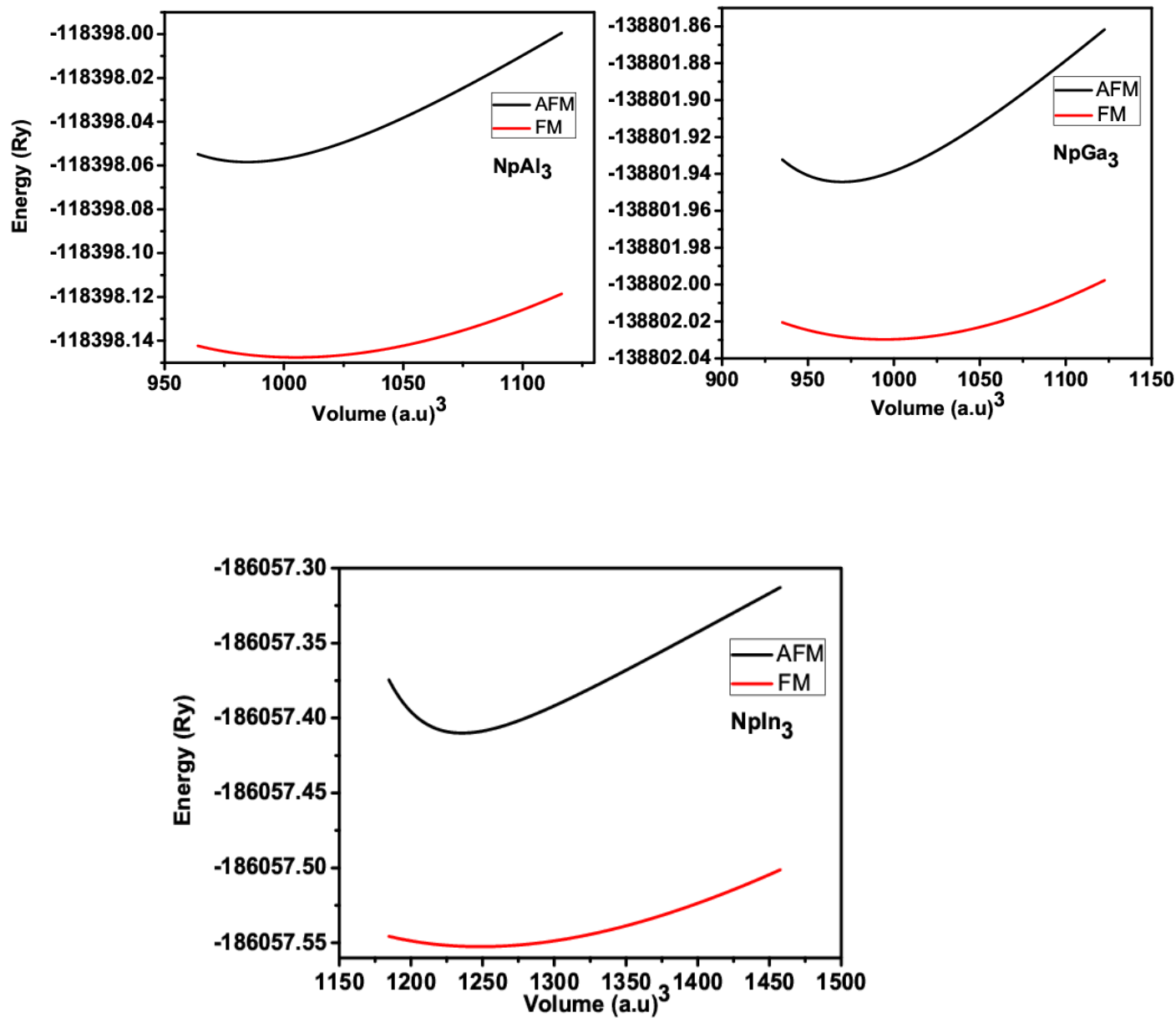


Figure 4. 4: (a, b, c). The change in total energy versus unit cell volume of NpPx_3 ($\text{Px} = \text{Al}, \text{Ga}, \text{In}$) under the GGA (PBEsol) functional.

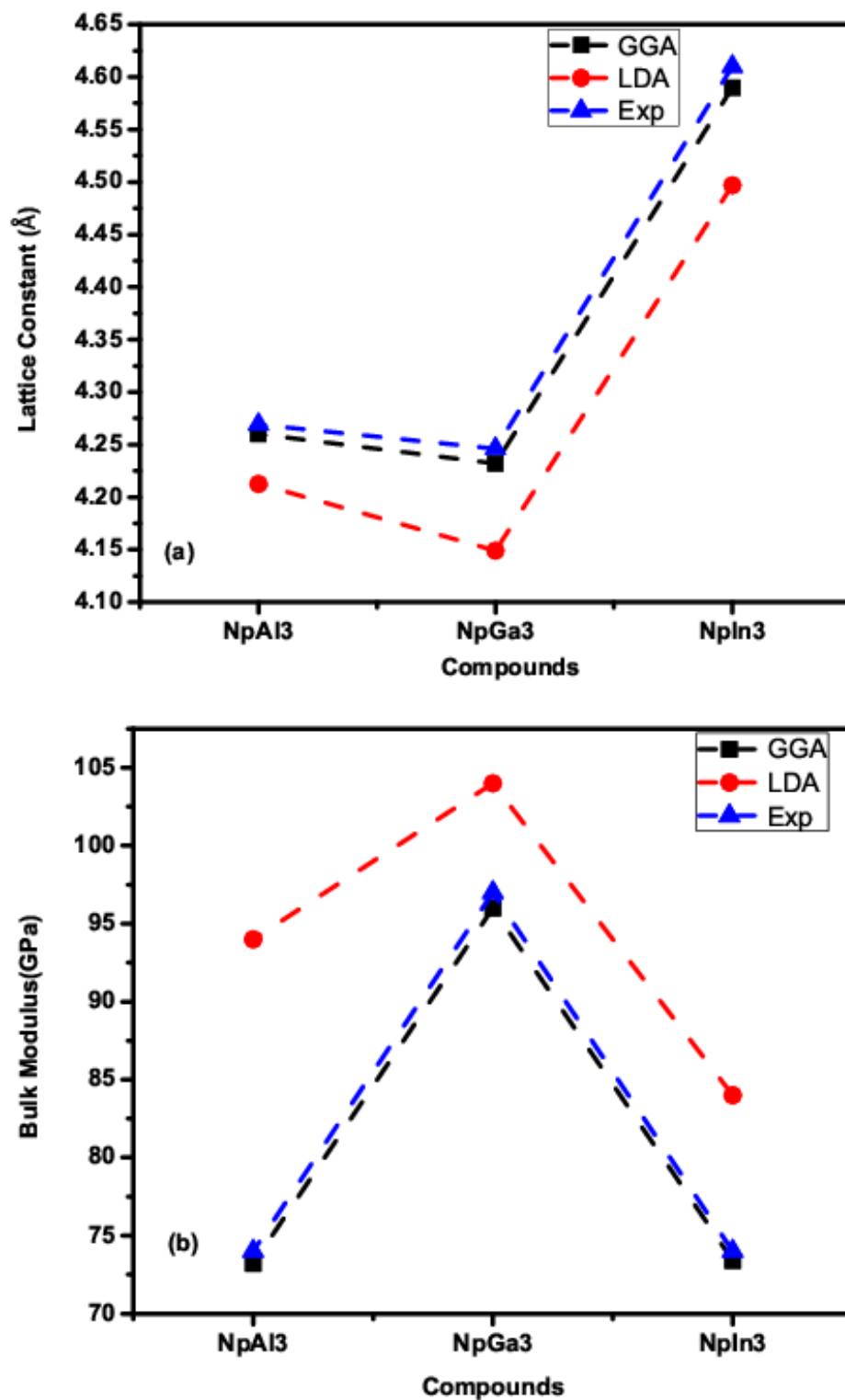


Figure 4.5: (a, b). Experimental, LDA and GGA lattice constant as well as bulk modulii of cubic NpPx₃ (Px= Al, Ga, In) intermetallic compounds.

4.2.2 Magnetic Nature of NpPx_3 ($\text{Px}=\text{Al, Ga, In}$)

The magnetic behavior of NpPx_3 [$\text{Px} = \text{Al, Ga, In}$] is controversial at various temperature due to its 5f- electrons therefore its detailed study is necessary to clarify the ambiguity. As these materials are heavy fermion in nature therefore we used spin orbit coupling (SOC) calculations. The magnetic moment is calculated by GGA-(PBEsol) which is underestimated. This is due to well known self-interaction error (SIE) contained in LDA and GGA functionals. The results are also checked by GGA (PBEsol) + U with addition of different values of U from 2 to 11 eV as shown in Fig. 4.6 (a) but the results were still not satisfactory. The d and f orbitals are heavy fermions therefore SOC calculations may be significant in these materials. The SOC calculations are very essential to calculate orbital, spin and total magnetic moments of atoms. Our evaluated values of orbital spin and net magnetic moments for NpPx_3 by GGA-(PBEsol), GGA-(PBEsol) plus U and HF-(PBEsol) in addition to experimental results are shown in Table 4.8. The HF-PBEsol scheme gives the total magnetic moments of neptunium atom to be $1.6 \mu_B/\text{Np}$ (NpAl_3), $1.64462 \mu_B/\text{Np}$ (NpGa_3) and $1.59289 \mu_B/\text{Np}$ (NpIn_3) which is consistent with the experimental results of Oddou *et al* [23] Sanchez *et al* [22] and Colineau *et al* [200].

The HF-PBEsol with SOC improves the magnetic moment of Np, which means that hybrid functionals is better for the treatment of 5f- state electrons. Our results show that NpPx_3 has minimum ground state energy at ferromagnetic phase. So these materials are intermetallic ferromagnetic having large orbital moment aligned antiparallel to the spin moment of f-states electrons and valence as well as conduction band crossing the Fermi level as shown in Fig. 4.7 (a, b, c, d, e, f) at very low temperature. The actinide 5f- electrons hybridize with ligand orbitals

and play a crucial role in establishing magnetic nature of NpPx_3 . The central contribution arise in spin magnetic moment of neptunium atom is due to the non-spherical $5f^{+3} [\text{Np}^{+3}]$ orbital electrons. The Al post transition metals magnetic moment is very small due to less orbital and spin angular momentum of s- and p- states of electrons. The Ga and In magnetic moment are also small due to filled d-states and less amount of orbital and spin angular momentum of s and p states. The Np have unfilled d and f states electrons which have large spin and orbital magnetic moments but both are oriented in opposite direction in the NpPx_3 so its resultant magnetic moment is small. It means the electrons are overlapping each other. There are two probable overlapping of electrons in such compound, the hybridization of 5f- electrons with p and direct 5f-5f which causes the intermetallic nature of these compounds, moreover, due to the higher occupation of the p states as one moves from top to bottom in a group IIIA, the f-p hybridization is favored.

The inter-atomic actinide-actinide distance has been calculated as shown in Table 4.7. In terms of *Hill limits*, [34, 201] it turns out that d (Np-Np) is remote from Hill limits $\approx 3.25\text{\AA}$ in NpPx_3 , therefore it is concluded that 5f ligand hybridization is the central mechanism for controlling the delocalization of 5f electrons and the large value confirms the ferromagnetic behaviour of NpPx_3 . It is clear from Table 4.8, that the orbital and spin magnetic moment ratio (μ_l/μ_s) almost remains constant for Np and Px by using different functionals.

Table 4.8: Calculated spin (μ_{spin}), orbital (μ_{orb}) and total magnetic moment ($\mu_{\text{tot}}=\mu_{\text{orb}}+\mu_{\text{spin}}$) in terms of Bohr magneton (μ_B) of NpPx_3 ($\text{Px} = \text{Al, Ga, In}$) by using different exchange potential with spin orbit coupling calculation.

Compounds	LDA	GGA (PBEsol)	GGA+U U= 7 eV	HF α 0.10	Experimental μ_{total}	Ordering Tem (K)
NpAl_3					1.3 ^[23]	62.5 ^{F[23,33]}
μ_s	3.2567	2.9544	3.6220	2.8446		
μ_{orb}	-4.0532	-2.9130	-4.4991	-4.4560		
μ_{tot}	-0.7965	0.0414	-0.8771	1.6114		
μ_l/μ_s	1.2400	0.9800	1.2400	1.5600		
NpGa_3					1.56 ^[22]	4.2 ^{F[22]}
μ_s	3.0758	2.9597	3.7408	2.8687		
μ_{orb}	-3.6288	-2.9112	-3.4865	-4.5133		
μ_{tot}	-0.5529	-0.0485	0.2543	1.6446		
μ_l/μ_s	1.1700	0.9800	0.9300	1.5700		
NpIn_3					1.4 ^[22]	10 ^{F[22-200]}
μ_s	3.3414	3.3015	3.7747	3.3445		
μ_{orb}	-4.0540	-3.4953	-3.6157	-4.9374		
μ_{tot}	-0.7125	-0.1937	0.1590	1.5928		
μ_l/μ_s	1.2100	1.0600	0.9500	1.4700		

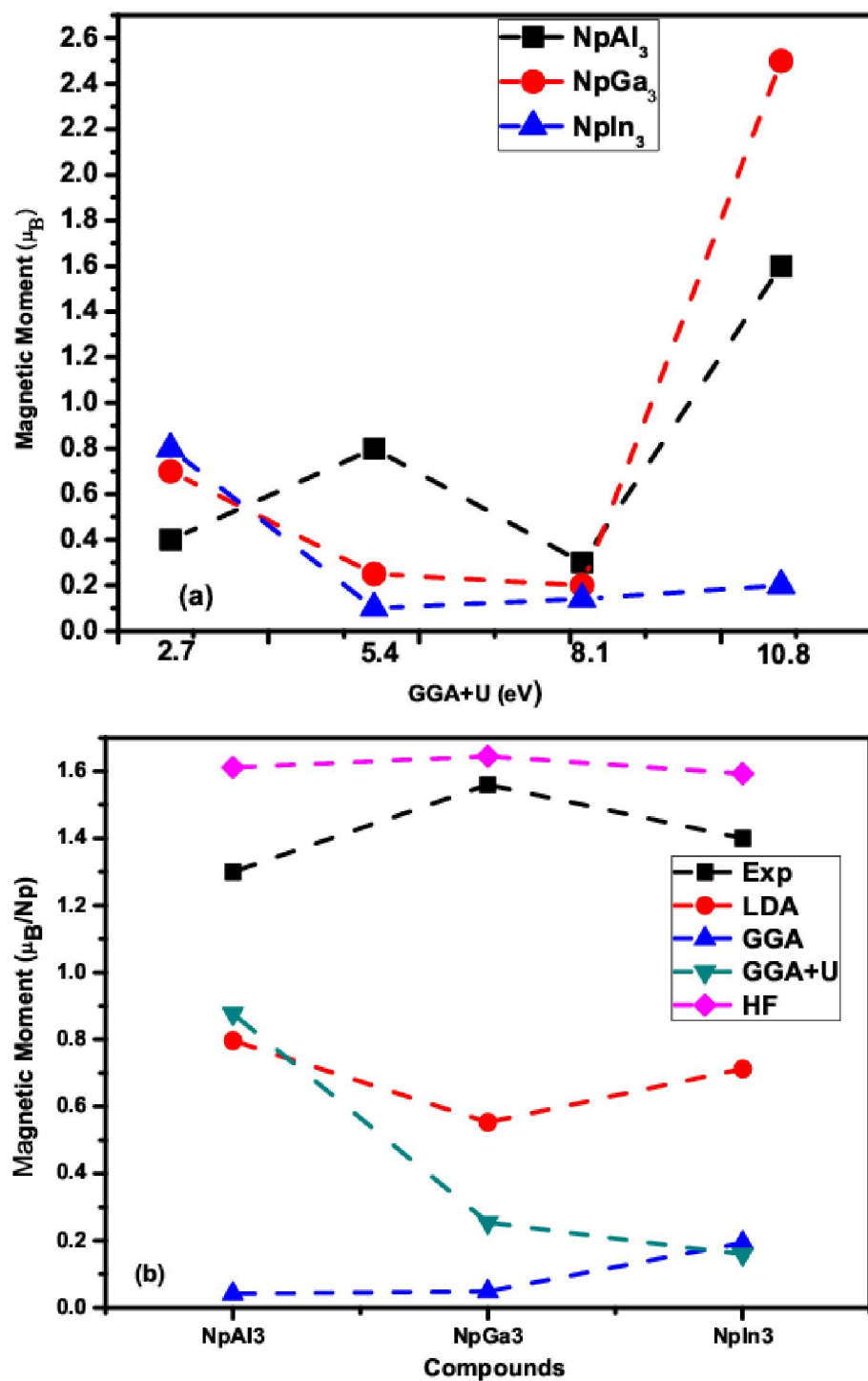


Figure 4.6: (a, b). Calculate magnetic moment of NpPx_3 by using different values of U .

(b) Experimental as well as calculated magnetic moment for NpPx_3 series.

4.2.3 Electronic and Specific Heat of NpPx₃ (Px=Al, Ga, In)

The information of specific heat nature at low temperature is a significant feature to understand the behavior of the compounds. In order to examine the electronic specific heat coefficient or Sommerfeld coefficient (γ) in NpPx₃ intermetallic compounds, we evaluated the DOS of NpPx₃. The electronic specific heat is connected to the DOS in a conventional metal about the Fermi energy level via following formula;

$$\gamma = \frac{\pi^2}{3} k_B^2 \text{Dos}(E_F) \quad 4.7$$

where k_B is the *Boltzman's* constant and $\text{Dos}(E_F)$ is the density of states at the Fermi energy [202]. These materials are intermetallic in nature, and all orbitals are contribute in bonding formation and there is hybridization between post transition metals aluminum, gallium and indium 3p, 4p and 5p with neptunium 5f states which leads to overlapping of valence and conduction band and present itinerant 5f states. It is observed that SOC spin polarized calculations have significant effects on the results and should be considered for heavy fermions compounds. All the calculated electronic specific heat for NpPx₃ are shown in Fig 4.7 (a, b, c, d, e, f).

The results of calculated values of specific heat of electron are given in Table 4.9, using hybrid functionals in presence and absence of SOC calculations. The addition of SOC increases DOS at Fermi level that improve γ value. The calculated electronic specific heat coefficient with HF-PBEsol+SOC is closer to experimental value [67-195]. The experimental electronic specific heat coefficient of atomic neptunium atom is 14.2 mJ/mole K² [203]. The experimental electronic specific heat coefficient of atomic neptunium atom is 14.2 m J/mole K² [48]. The

electronic specific heat coefficient of NpPx_3 ($\text{Px} = \text{Al, Ga, In}$) have been calculated computationally.

As shown in the Fig. 4.7 (a, b, c, d, e, f), that f state cross the Fermi level which confirms the intermetallic nature of the NpPx_3 . The electronic specific heat major contributed by 5f- states electrons. The calculated γ values are 78.2, 85 and 62 mJ/mol K^2 for NpPx_3 ($\text{Px} = \text{Al, Ga, In}$) by using HF-PBEsol with SOC. As shown in Fig.4.7, that valence band usually contributed by core electrons whereas conduction is due to unfilled d- and f-states electrons as well as d-and p states hybridization. The overlapping of conduction as well as valence band again verified the metallic and non-localized nature of 5f- states electrons in NpPx_3 . The large values of γ rather propose the presence of narrow 5f or 5f-6d bands at the Fermi level.

Table 4.9: The electronic specific heat ($\text{mJ mol}^{-1} \text{K}^{-2}$) in absence and presence of SOC of NpPx_3 ($\text{Px} = \text{Al, Ga, In}$).

	NpAl_3	NpGa_3	NpIn_3
Exp		100.0 ^[2]	72.00 ^[21]
HF-PBEsol	64.00	74.40	53.00
HF-PBEsol-SOC	78.20	85.00	62.00

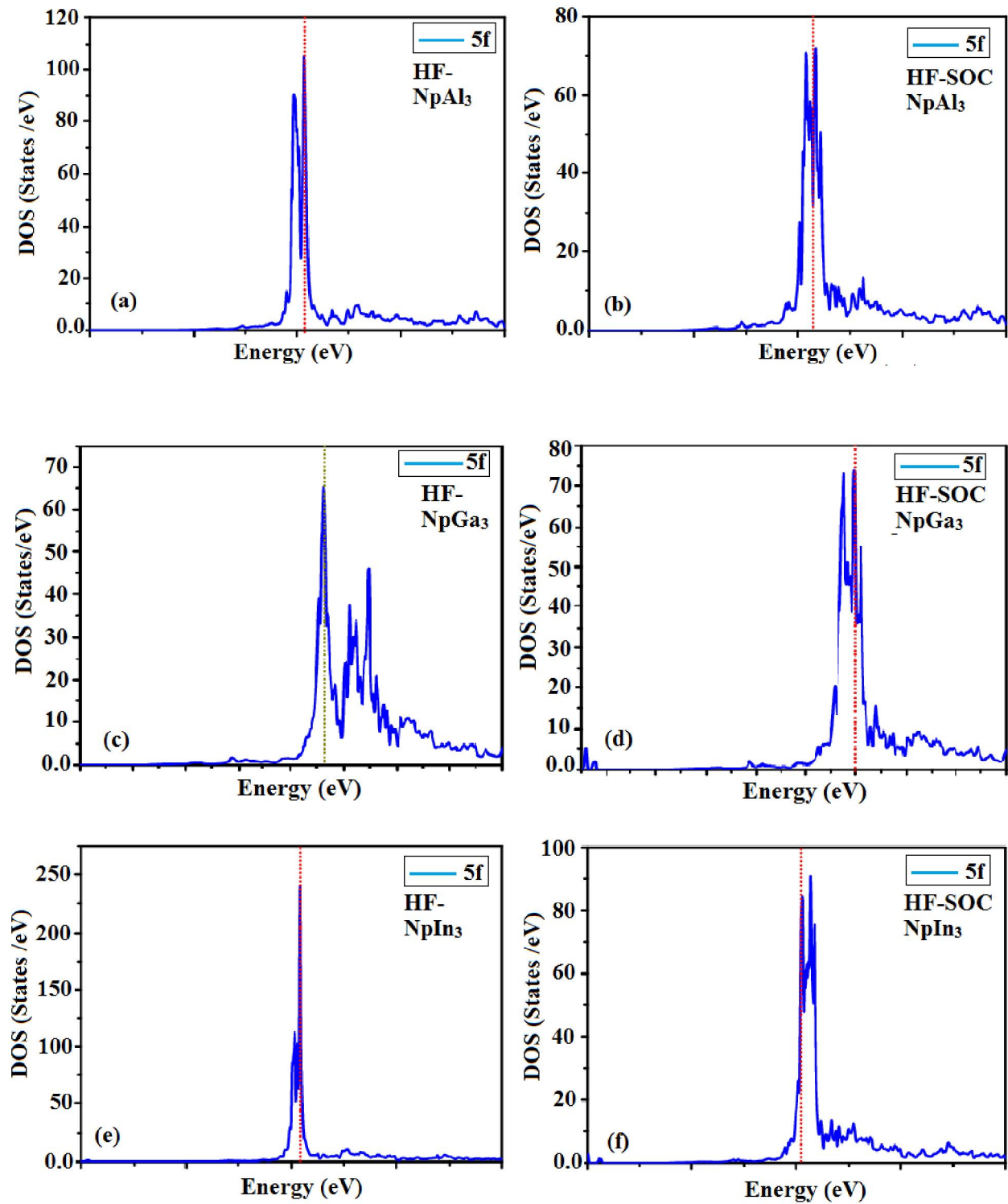


Figure 4.7: (a, b, c, d, e, f) The computed electronic density of states of NpPx_3 by hybrid functional with PBEsol in absence and presence of SOC. The vertical dashed line indicates the Fermi level.

4.2.4 Electric Field Gradient (EFG) of NpPx_3 (Px=Al, Ga, In)

EFG is a neighboring property of substance and mathematically, it is the second partial derivative of the electric potential calculated at position of the nucleus. It is a second rank tensor. The most informative component of EFG is V_{zz} which can be obtained from the potential expansion inside the muffin-tin spheres [83, 174]:

$$V_{zz} = \lim_{r \rightarrow 0} \left[\frac{5}{4\pi} \right]^{1/2} \left[\frac{V_{20}(r)}{r^2} \right] \quad 4.8$$

It is clear from equation (4.8) that the most important component of EFG tensor align to the z-axis, the other important parameter radial electric potential V_{20} , can be calculated as

$$V_{20}(r = 0) = \frac{4\pi}{5} \int_0^{R_{MT}} \frac{\rho_{20}}{r} dr - \frac{4\pi}{5} \int_0^{R_{MT}} \frac{\rho_{20}}{r} \left(\frac{r}{R_{MT}} \right)^5 dr \\ + 4\pi \sum_k V(k) J_2(kR_{MT}) Y_{20}(\hat{k}), \quad 4.9$$

where equation (4.9) consist of valence and lattice EFG. The first term of the equation (4.9) is contributed by the valence electron of the atomic sphere while the other terms exhibit the contribution of lattice part of the atomic sphere. As the atomic sphere have three dimensional geometry, so $J_2(kR_{MT})$ specify Bessel function in spherical coordinate with radius R_M and the other term ρ_{20} show density of expansion with $L = 2$ and $M = 0$. The EFG of individual atom varies from materials to material. It means that the EFG for a definite atom can be negligible or zero in one compound, while it can be non-zero and large in another compound, therefore EFG

can be considered as the fingerprint for each substance [175]. In most compounds or in a crystal, a gradient of the electric field surrounding nuclei and electrons interacts with nuclear quadrupole moment. This interaction has large importance in experimental methods such as, Nuclear Magnetic Resonance (NMR), Nuclear Quadrupole Resonance (NQR) and Mössbauer spectroscopy and High resolution techniques. The Quadrupole coupling interactions can be determined in NMR spectra in the form of line broadening [141, 176].

The central component of EFG V_{zz} cannot measurable by direct experiment. Experimentally it is calculated indirectly from a mathematical equation $E = C_Q h$. By matching the computational V_{zz} and experimental energy the quadrupole moment (Q) of the nuclei can be obtained. This is simple way to measure nuclear parameter Q.

It was found that the EFG is a very sensitive probe of the anisotropy of the charge densities around the nuclei. Electric field gradient of actinide NpPx_3 ($\text{Px} = \text{Al}, \text{Ga}, \text{In}$) has been examined by using different potentials like GGA and LDA+SOC. The calculated total V_{zz} , quadrupole coupling constant and interaction energy at actinide Np and Al, Ga and In sites in NpPx_3 ($\text{Px} = \text{Al}, \text{Ga}, \text{In}$) within different functional are tabulated in Table 4.10. The positive EFG values of actinides as well as Al, Ga and In exhibit prolate distribution of electrons. It is noticed that the s- and p- contributions in EFG of Np in NpPx_3 ($\text{Px} = \text{Al}, \text{Ga}, \text{In}$) are small compared to incomplete d- and f-orbital contributions. In NpPx_3 ($\text{Px} = \text{Al}, \text{Ga}, \text{In}$) Ga and In atom has 3d- and 4d- complete shell, and thereby the d orbital is nearly spherical symmetric. The total EFG of Np in NpPx_3 is positive which predicts the prolate shape. The total EFG of Np atom in NpAl_3 , NpGa_3 and NpIn_3 at actinide sites are $1.1681 \times 10^{21} \text{ V/m}^2$, $1.2276 \times 10^{21} \text{ V/m}^2$ and $1.3234 \times 10^{21} \text{ V/m}^2$ as shown in Table 4.10. The calculated values by different functionals are close to experimental value [21-23].

The Quadruple coupling constant ($C_Q = eV_{zz}Q/h$) [204] is a main parameter utilized for the purpose to compute Mössbauer quadrupole splitting in the compounds. The C_Q connects the interaction energy between the nuclear electric quadrupole moment (eQ) and the principle component of EFG at the sites of the quadrupole nuclei. The nuclear electric quadrupole moment of the ^{237}Np , ^{27}Al , ^{69}Ga and ^{115}In are 3.866, 0.27(3), 0.171(5) and 0.77(5) barn respectively [179]. The nuclear quadruple resonance (NQR) parameter, quadrupole coupling constants C_Q of NpPx_3 ($\text{Px} = \text{Al}, \text{Ga}, \text{In}$) have been computed computationally for the first time for Np, Al, Ga and In atom may have very considerable character in NMR literature and spectroscopy. The 5f and 6p states of Np majorly contributed in the interaction energy in NpPx_3 intermetallic compounds due to its diffuse nature around the nucleus sites.

The C_Q of Np in NpAl_3 108, NpGa_3 114 and NpIn_3 are 123 MHz. The foremost contribution in C_Q is owing to valence non-spherical V_{zz}^{f-f} and V_{zz}^{d-d} EFG. As shown in Fig.4. 8, the V_{zz} , C_Q as well as interaction energy increase from Al-In compounds, this due to varying number of fermions and atomic size of group IIIA elements (Al, Ga, In). The quadrupole interaction energies at, Np in NpPx_3 are due to the result of electric quadrupole moment of nuclei and its valence EFG of 6p and 5f electrons, while in case of Ga and In the interaction is due to the d- and p- state electrons. The quadrupole interaction in micro electron volt increases from aluminum to indium at both neptunium and post transition metal atomic site in NpPx_3 family as shown in Table 4.10, this increase is due to increase of p- orbital as well as different electronegativity from aluminum to indium.

Table 4.10: Electric field gradient in $10^{21} \times \text{V/m}^2$, and NMR parameter coupling constant C_Q of intermetallic NpPx_3 ($\text{Px} = \text{Al, Ga, In}$) compounds by using GGA (PBEsol) and LDA in the presence of SOC calculations.

Compo-	GGA- V_{zz}	LDA- V_{zz}	Exp- V_{zz}	Exp- C_Q	C_Q (MHz) GGA	C_Q (MHz) LDA	LDA+SO (μeV)
NpAl₃							
Np	1.0376	1.1681	1.13 ⁽²³⁾	105.64 ⁽²³⁾	99.0	108	0.45
Al	2.6730	2.8323			17.0	18.0	0.07
Al	2.7032	2.8872			18.0	18.0	0.07
NpGa₃							
Np	1.1374	1.2276	1.59 ⁽²¹⁾	148.86 ⁽²¹⁾	105	114	0.47
Ga	8.6773	9.0879	---	---	35.0	37.0	0.15
Ga	8.7544	9.2191	---	---	36.0	38.0	0.15
NpIn₃							
Np	1.2980	1.3234	1.51 ⁽²³⁾	139.25 ⁽²³⁾	121	123	0.51
In	13.636	14.332	---	---	253	266	1.10
In	13.567	14.305	---	---	252	268	1.10

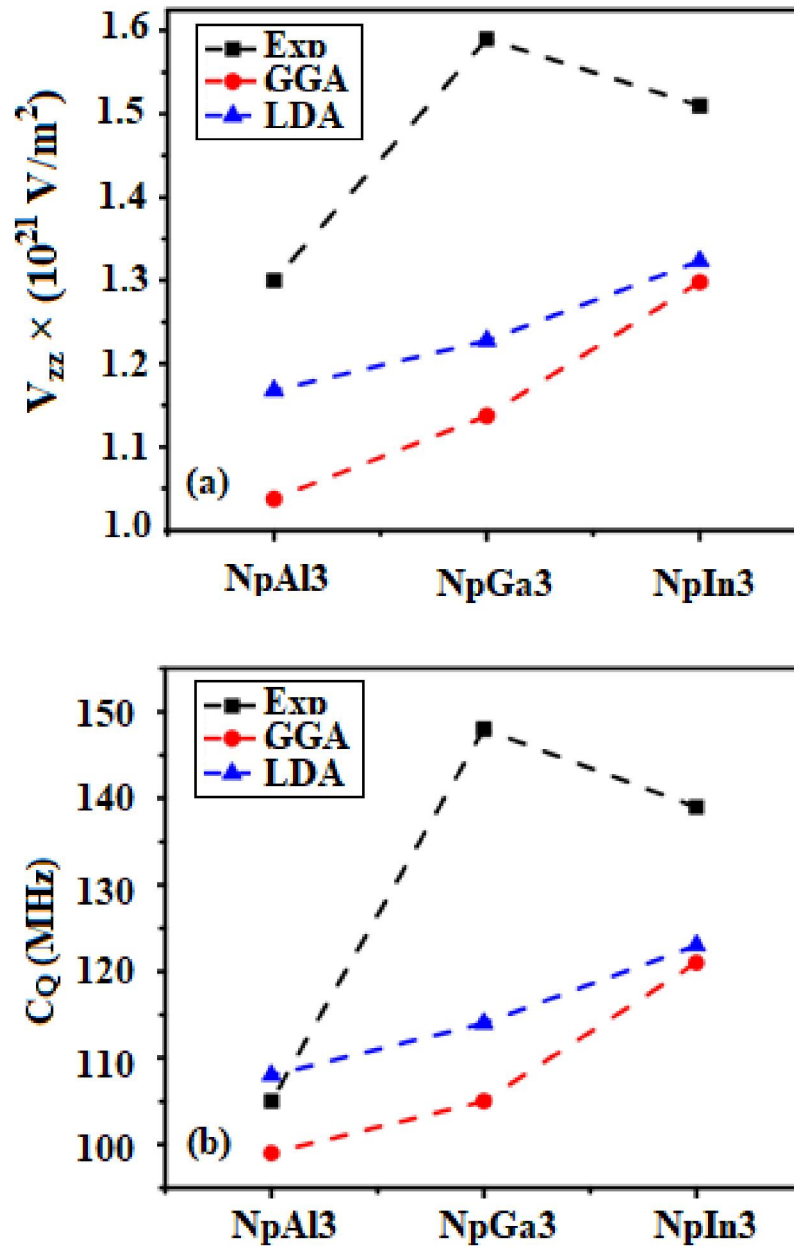


Figure 4.8: (a). Calculated principle component of EFG for NpPx₃ (Px= Al, Ga, In) (b) and quadrupole coupling constant in MHz for NpPx₃.

4.3 Theoretical Studies of UX_3 ($X = \text{In, Tl, Pb}$) Compounds

The AuCu_3 type cubic uranium like, UGe_3 , USi_3 , USn_3 , UAl_3 , UIn_3 , UTl_3 and UPb_3 are intermetallic compounds. These compounds exhibit some remarkable properties like, Pauli paramagnetism UY_3 ($Y = \text{Si, Ge}$), unconventional superconductivity, spin fluctuation UZ_3 ($Z = \text{Al, Sn}$) and antiferromagnetism UX_3 ($X = \text{In, Al, Ga}$). The extensive properties of these compounds are due to their 5f- electrons. The 5f- electrons exhibits dual character, sometime it behaves like localized while in many cases it shows non-localized electronic nature. The diverse 5f- properties are due to the wide extension of 5f- electrons [10].

These compounds have cubic structure. The inter-atomic separation between the uranium is equal to the lattice constant of the unit cell. The inner separation value between U- and U-atom is far away from the Hill limit (3.25 — 3.5 Å). This show that there are 5f- ligand hybridization occur which is the central mechanism of controlling the 5f- electrons [14, 27]. Hill *et al* [34] studied that protactinium Pa element is the primary atom of actinide series and concluded that 5f- electrons exhibits itinerant nature. Kmetko *et al* [205] and Johansson *et al* [206] studied that the actinide series have some heavy atoms; they concluded that americium is the first heavy element of the series which have localized electrons, thus Am is the starting heavier atom of the series and exhibit rare earth metallic nature.

The electronic specific heat which exhibits the density of states of electron around the Fermi level is also an important parameter. The actinide atoms are mostly intermetallic so the electronic specific heat values for these compounds are very prominent. Maaren *et al.* [62] and Tokiw *et al.* [209] studied experimentally the electronic specific heat of UIn_3 and UPb_3 and concluded its values are $50 \text{ mJ/K}^2 \text{ mol}$ (UIn_3) and $110 \text{ mJ/K}^2 \text{ mol}$ (UTl_3) [20, 210]. The magnetic nature of UX_3 ($X = \text{In, Tl, Pb}$) has been studied by Murasik *et al.* [16-17, 61] experimentally by

neutron diffraction method and observed the magnetic moment for UIn_3 $1.0 \mu_B$, UTl_3 $1.6 \mu_B$ and UPb_3 $1.7 \mu_B$. Murasik *et al.* concluded the antiferromagnetic nature of these compounds. Tokiwa *et al.* [209] also studied these compounds and found the antiferromagnetic nature with Néel Temperature 80 K, 90 K and 30 K for UIn_3 , UTl_3 and UPb_3 respectively.

The electric field gradient (EFG) is one of the interesting parameter which exhibit the deviation of electronic cloud around the nucleus has numerous applications in nuclear physics as well as condensed matter physics. EFG behave like a bridge between condensed matter physics and nuclear physics. Recently Yazdani-Kachoei *et al.* [140], Ghasemikhah *et al.* [154] and Jalali *et al.* [141] investigated the EFG of heavy fermions CeIn_3 , uranium dipnictides.

In current thesis we explored the different properties like structural, electronic, magnetic and EFG, quadrupole coupling constant as well as hyperfine field and its types, orbital, dipolar and Fermi contact of these compounds by using different functional like LDA, GGA, GGA plus U and hybrid functional in the absence and presence of SOC calculations.

4.3.1 Structural Properties of UX_3 ($\text{X} = \text{In, Tl, Pb}$)

The whole family of UX_3 [$\text{U} = \text{In, Tl, Pb}$] compounds exhibit the face centered cubic structure with lattice constant $4.601 \text{ \AA}$ (UIn_3), $4.674 \text{ \AA}$ (UTl_3) and $4.792 \text{ \AA}$ (UPb_3) respectively. The atomic position of uranium is 1 (a); (0, 0, 0) while In, Tl and Pb are 2 (d); (0.5, 0.5, 0.0); (0.0, 0.5, 0.5) and (0.5, 0.0, 0.5) with space group Pm-3m (221) [20, 27].

We optimized the unit cell volume of UX_3 versus energy by LDA and GGA approximation and fitted the results in famous Birch-Murnaghan equation of states [166]. The structural properties like, lattice constant, bulk moduli, derivative of bulk moduli, volume, inter-atomic separation between U-U and U-X have been calculated in optimized state. All the

calculated data tabulated in form of Table 4.11. The optimized graphs of energies (Ry) versus volume (a.u)³ is shown in Fig 4.9 (a, b, c). We used first the LDA to find the structural properties but our result underestimates due to the well known self interaction error and uniformly treats the electronic cloud [197-198]. The LDA shows the over binding tendency among the UX₃. The actual picture of electronic distribution is very different from LDA. The electronic density is not uniform around the nucleus so we used the second approximation GGA which treat the electronic cloud non uniformly, the results are very fruitful and there are only 1%, 0.6 % and 1.5 % error between experimental and our theoretical values. The results of GGA are better than LDA which are exhibited in Fig 4.10 (a).

The second important parameter of structural properties is bulk moduli which exhibit the strength of the material have been calculated for UX₃ by LDA and GGA. As show in Fig 4.10 (b) the bulk moduli decrease when one move from UIn₃ to UPb₃ while the lattice constant increase. This means hardness decrease in UX₃ family when one move from indium to lead in UX₃ family. There is an inverse relation between lattice constant and bulk modulus. Both LDA and GGA confirm indirect relation between lattice constant and bulk modulus as shown in Table 4.11.

The other important parameter of structural properties is pressure derivatives B' which have lot of application in high temperature physics [199] have been calculated for the first time. The UIn₃ shows largest value of pressure derivatives B'.

To clarify the magnetic nature of UX₃ family we optimized the double cell volume and point out that UIn₃, UTe₃ and UPb₃ have lowest energy in antiferromagnetic phase which magnitude are -182871.984323 Ry, -355705.196109 Ry and -363380.838078 Ry. The inter-ionic separation between the U-U is equal to the lattice constant of unit cell, which is very far away from Hill limit. The larger value than Hill limit exhibits that the f-f hybridization diminish

among uranium atoms while the f-spd hybridization dominant. The computed bond length between U-X and U-U consistent with available results [14, 27]. The U-In bond length in the series is less than the U-Tl and U-Pb which lead to more hardness and larger bulk modulus. It has been computed that smaller the bond length between U-X greater will be the bulk modulus in UX_3 family, as shown in Table 4.11.

Table 4.11: Comparison of computational and experimental optimized structural properties like, lattice constant, inter atomic space, bulk moduli, derivative of bulk moduli, double cell ground state energy in the unit of (Å), (GPa) and (Ry).

	LDA	GGA (PBsol)	Exp	% err GGA
UIn ₃				
Lattice	4.499402	4.547502	4.601 ^{14, 27}	1%
Pressure	89.11310	79.95341		
Volume	91.088554859784	94.041191546875	97.399493801	3.4%
P derivative	5.00	5.00		
Ferro		-182871.945423		
Anti-Ferro		-182871.984323		
U-U			4.601 ^{14, 27}	
Exp U-In			3.253 ^{14, 27}	
GGA U-U		4.6021		
GGA U-In		3.2541		3.253
UTl ₃				
Lattice	4.594510	4.64210	4.674 ^{14, 27}	0.6%
Pressure	84.13950	76.3551		
Volume	96.987277283625	100.033041876462	102.10949402	2.0%
P derivative	5.00	5.00		
Ferro		-355705.144265		
Anti-Ferro		-355705.196109		
U-U			4.674 ^{14, 27}	
Exp U-In			3.306 ^{14, 27}	
GGA U-U		4.67401		
GGA U-Tl		3.30502		
UPb ₃				
Lattice	4.668810	4.715801	4.792 ^{14, 27}	1.5%
Pressure	77.2868	69.49121		
Volume	101.769071132672	104.873589868312	110.039961088	4.6%
P derivative	5.00	5.00		
Ferro		-363380.824292		
Anti-Ferro		-363380.838078		
U-U			4.792 ^{14, 27}	
Exp U-In			3.388 ^{14, 27}	
GGA U-U		4.7920000		
GGA U-Pb		3.3884602		

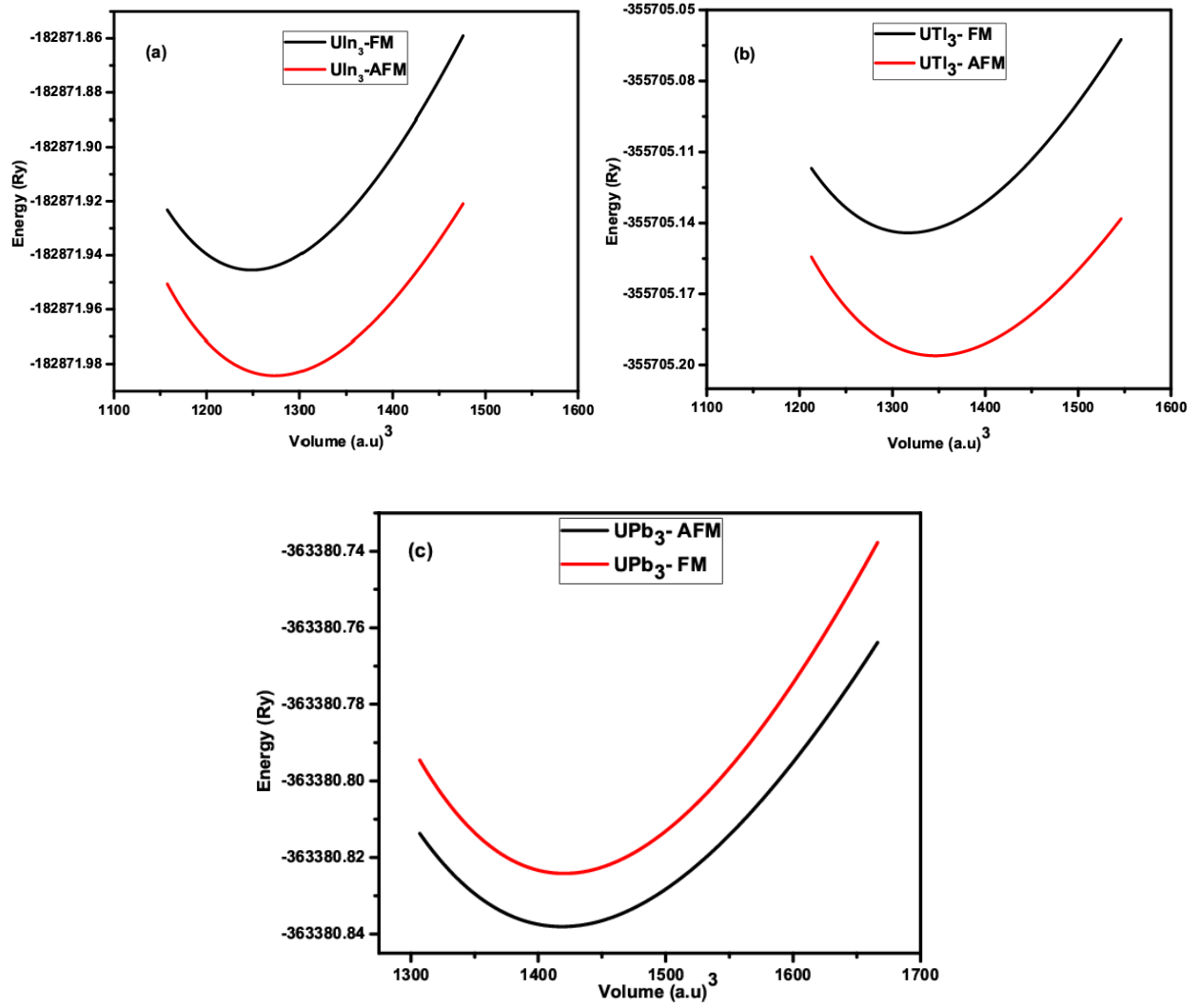


Figure 4.9: Double cell calculated energy (Ry) versus volume (a.u.)³ graph of actinide post transition metal UX₃ for clarification of ferromagnetic and anti-ferromagnetic structure.

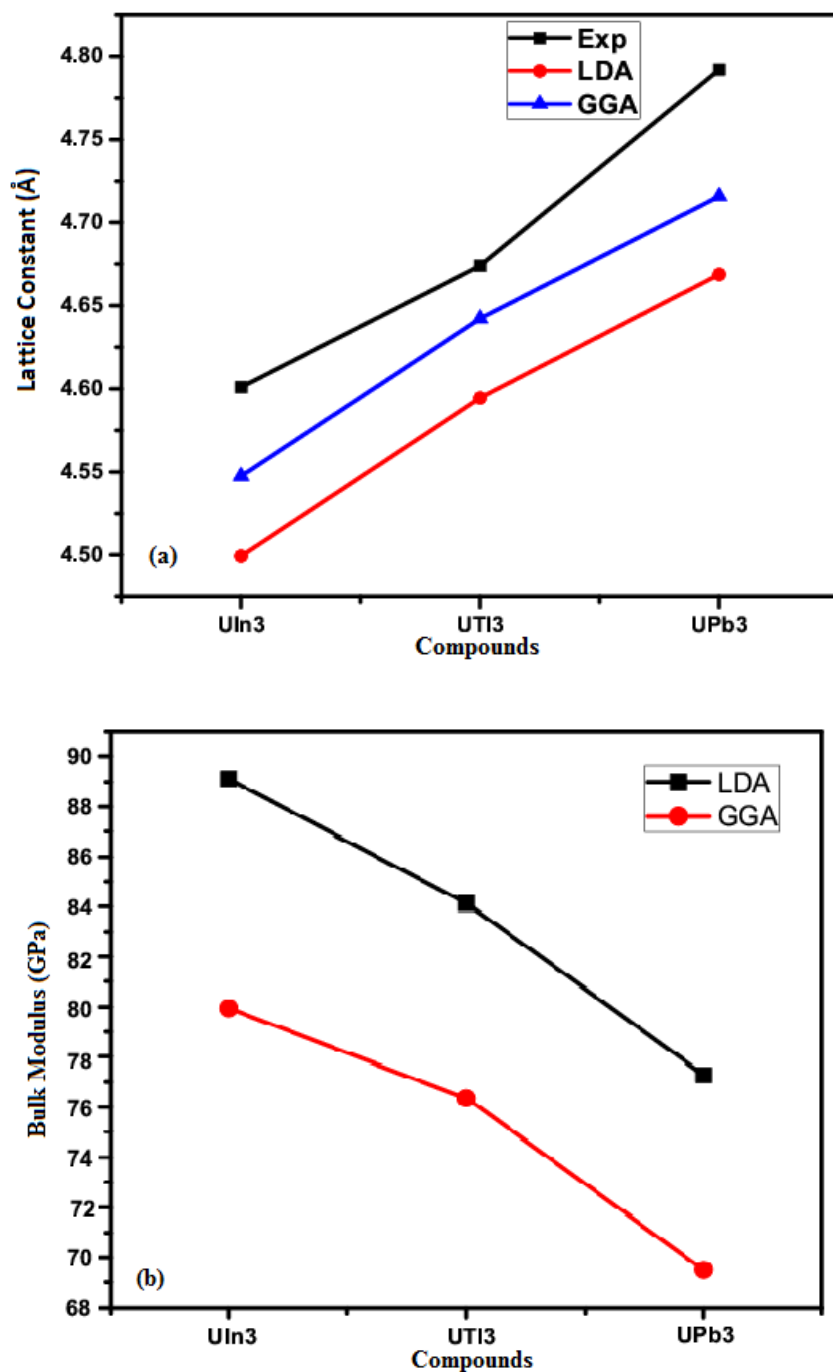


Figure 4.10: Comparison of theoretical and experimental (a) lattice constant in (Å) and (b) bulk moduli in (GPa) of UX₃ family under different exchange correlation functionals.

4.3.2 Electronic Specific Heat and Band Structure of UX_3

Band structure as well as Density of State (DOS) is one of the important parameter for clarification of insulating and metallic nature of an element or compound. In this part we computed the band structure as well as DOS of UX_3 compounds. The Band structure of UX_3 compounds have been evaluated under GGA+U with SOC. The calculated band structure shown in Fig 4.11 (a,b,c). The band structure graphs show that valence and conduction band cross the Fermi level which clarifies the intermetallic nature of UX_3 . The 5f- electrons of uranium are loosely bound which overlapping is maximum to the neighboring atom. It plays a crucial role in metallic nature of these compounds. Fig 4.11 (a,b,c) band structure exhibits that mostly the 5f- electrons contributed in intermetallic nature Fermi level. Electronic specific heat is one of the fundamental parameter in understanding the nature of an unconventional metal at low temperature. The electronic specific heat can be computed from the DOS. The electronic specific heat interrelated to the DOS by the following equation;

$$\gamma = \left[\frac{\pi^2}{3} DOS(E_F) k_B^2 \right] \quad 4.10$$

where $DOS(E_F)$ is the density of states around the Fermi level in states/eV [202] and k_B is the *Boltzman's* constant. We used different functionals like GGA with onsite Hubbard potential U and hybrid HF-PBEsol in the presence and absence of SOC effect. The SOC effect for electronic properties of uranium compound is very effective as shown in Fig 4.12. The electronic specific heat values for UIn_3 , UTl_3 and UPb_3 without SOC calculations are 33.12 mJ/mol K^2 , 108 mJ/mol K^2 , 57.5 mJ/mol K^2 respectively. By adding the SOC effect the calculated electronic specific heat or Sommerfeld coefficient are 55.5 mJ/mol K^2 , 122 mJ/mol K^2 and 114 mJ/mol K^2 which are very close to experimental results [62, 209-213] as shown in Table

4.12, hence SOC calculation treat well the heavy fermion and improve the value of electronic specific heat.

The partial orbital contribution to electronic specific heat exhibits in Fig 4.12. It is clear from Fig 4.12 that 5p- and 6p- orbitals contribute in indium, thallium and lead while the 5f- electrons involvement in uranium atom. As clear from Fig 4.12 there is a 5f- hybridization with ligand p- orbital. There is also an overlapping of 5f- electrons about the Fermi level which is the confirmation of intermetallic nature of UX_3 compounds. It is clear from Fig 4.12 that f- and p- orbital contributed in formation of conduction band while the core electrons contribution in valence band is dominant.

Table 4.12: The comparison of experimental and calculated electronic specific heats by GGA+U and HF-PBEsol in absence and presence of SOC calculations of UX_3 compounds.

Functionals	UIn ₃	UTl ₃	UPb ₃
GGA+U	32.20	55.21	7.012
HF- SOC	33.12	108.1	57.51
GGA+U	46.01	73.60	55.21
HF-	55.51	122.06	114.2
Exp. γ	50.03 ^[62,209]		110.00 ^[62,209]

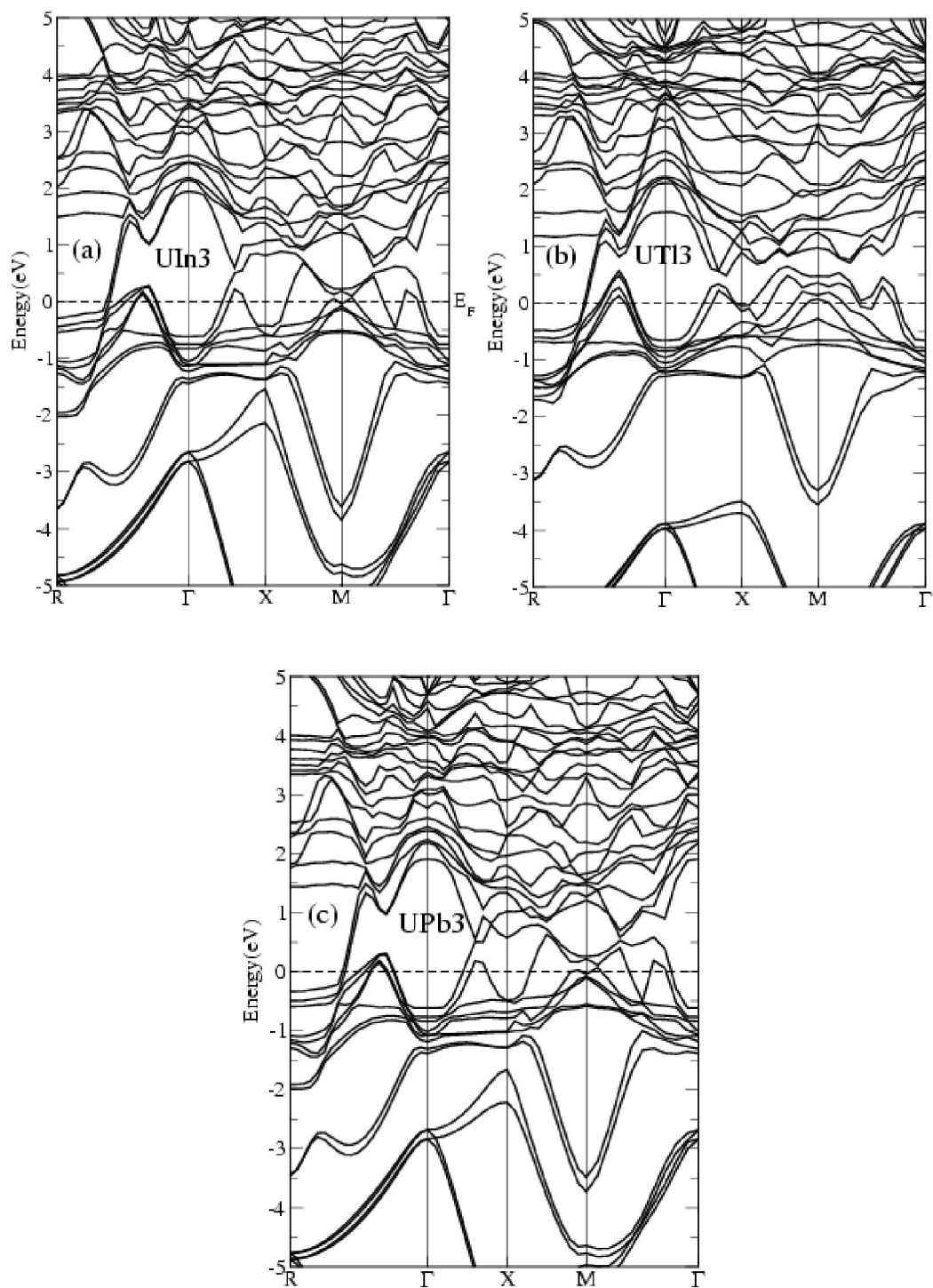
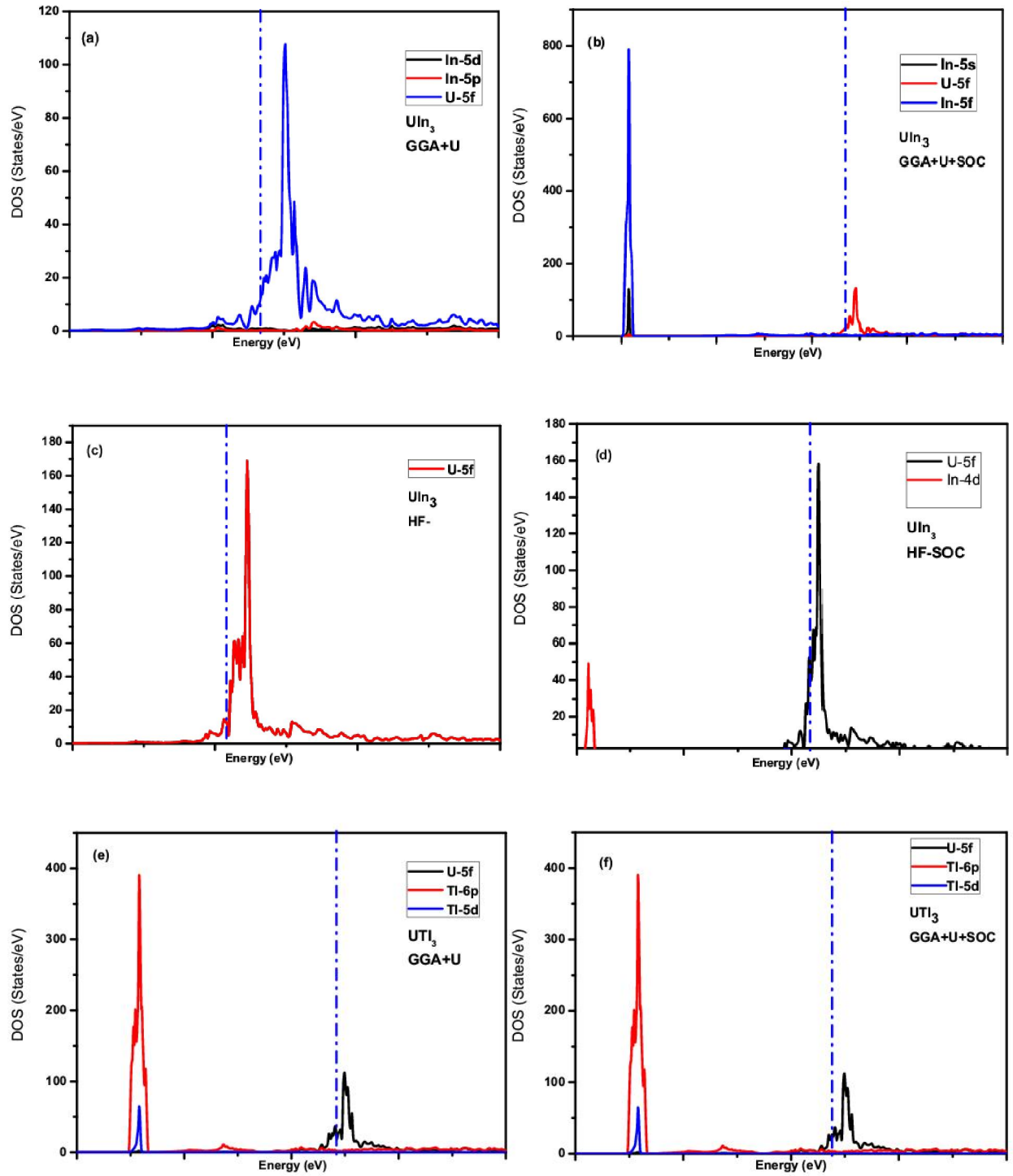


Figure 4.11: (a, b, c). Calculated electronic band structure of UX₃ compounds by GGA+U with SOC calculations.



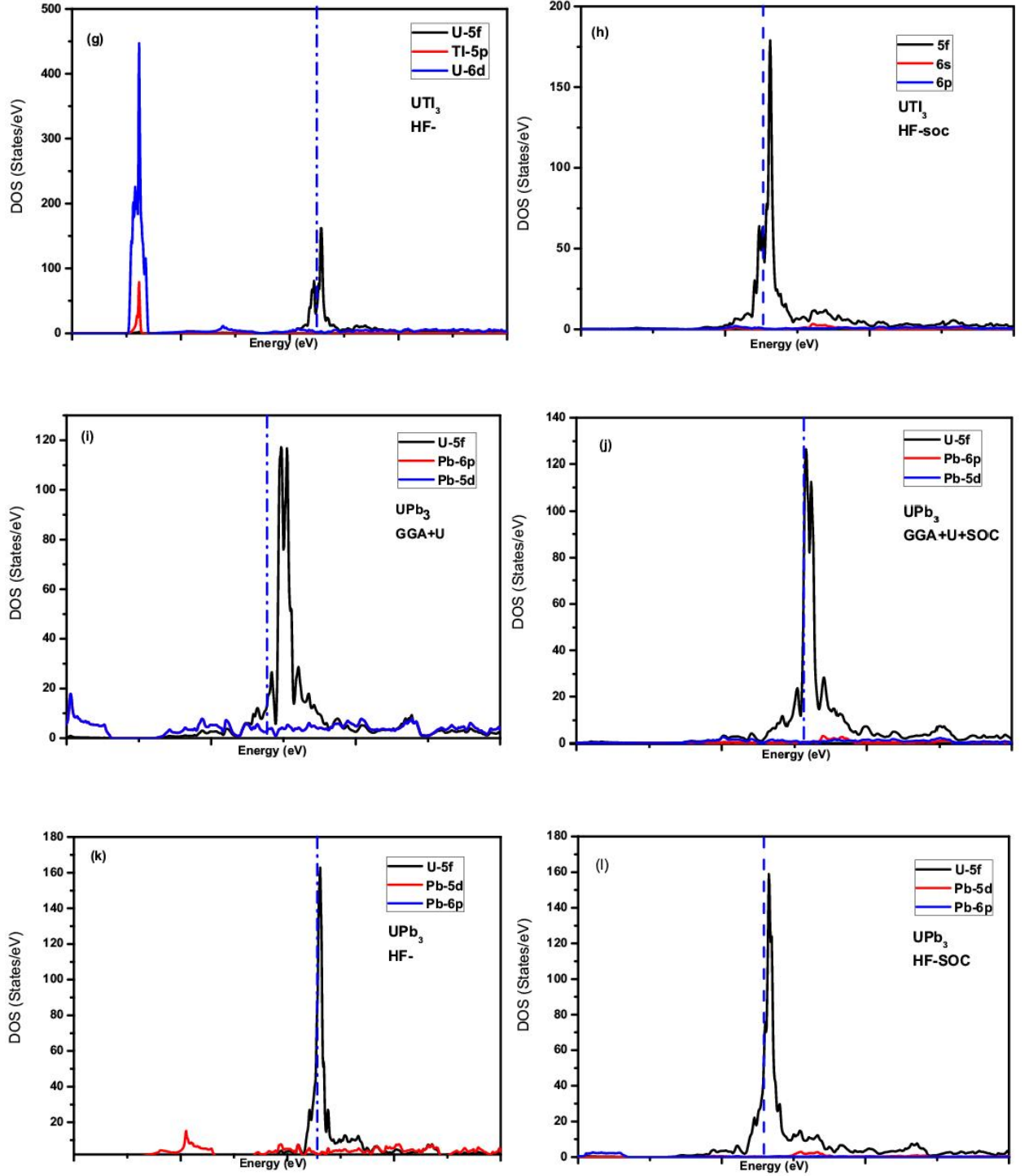


Figure 4.12: (a, b, c, d, e, f, g, h, I, j, k, l). The Computed energy versus DOS (States/eV) of UX_3 compounds by various functional. The dashed line shows the Femi energy level.

4.3.3 Magnetic Properties of UX_3 Compounds

The studies of magnetic properties of UX_3 compounds are very significant due to the dual nature of 5f- extended electronic wave function. The electronic configuration of uranium, In, Tl and Pb are $6p^6 5f^3 6d^1 7s^2$, $4p^6 4d^{10} 5s^2 5p^1$, $5p^6 5d^{10} 6s^2 6p^1$ and $5p^6 5d^{10} 6s^2 6p^2$ respectively. The bond formation of actinide compounds is due to the direct 5f- electrons overlapping to neighboring actinide atom as well as ligand s-, p- and d- orbitals. Different functionals like GGA plus U as well as hybrid HF-PBEsol are used to investigate the interstitial as well as spin magnetic moment at uranium, indium, thallium and lead sites. The Uranium has large number of electrons so there are strong spin and orbital angular momentum as well as magnetic moments interaction are expected. To calculate the orbital and total magnetic moment at uranium and post transition site SOC calculations also take into accounts [214-215].

The interstitial, individual uranium, indium, thallium and lead spin, orbital and total magnetic moment has been tabulated in Table 4.13. The calculated orbital and spin magnetic moment are antiparallel as a result net magnetic moment very small in magnitude. The calculated spin and orbital magnetic moment under SOC calculation fulfill Hund's third rule $J = |L - S|$. The calculated magnetic moment at uranium site in UIn_3 , UTl_3 and UPb_3 are $1\mu_B/U$, $1.4\mu_B/U$ and $1.6\mu_B/U$. This show that there are an increasing trend in the magnetic moment at uranium site, such a trend observed by Murasik *et al.*, [16-17] experimentally by neutron diffraction techniques. The regular increase trend in UX_3 is due to varying electrons in the outer orbitals, different lattice constant as well as different electronic environment around the uranium sites. It is concluded that total magnetic moment is directly related to the lattice constant in UX_3 family. The computed magnetic moment at individual sites can be summarized by following way. The orbital magnetic moment at uranium sites is larger in magnitude. The calculated spin magnetic

moment has small value. Both magnetic moments have opposite directions and symbols as a result the net magnetic moment reduced to small magnitude. The calculated magnetic moment at In, Tl and Pb site by different potentials is very small and both are oriented parallel to each but the resultant magnitude have very small value this due to the closed d- and unfilled p- orbital. It is concluded that magnetic character indium, thallium and originate due to 5p and 6p- electrons while 5f- show dominancy at uranium sites. The evaluated partial DOS around Fermi energy as exhibits in Fig 4.12 shows that uranium moment is almost exclusively of 5f- character and indium, thallium as well as lead moment is mainly originated by 5p- and 6p- characters.

The magnetic moment of uranium sites an individual unit cell in UX_3 compounds also shown in Fig. 4.13 (a) and Fig. 4. 13 (b). The calculated magnetic moments at uranium sites by different potential shows that GGA+U with SOC treat well the magnetic nature of UX_3 series. So we recommended such potential for calculation of magnetic moment in UX_3 family. The sum of U and X atom magnetic moment per unit cell has been computed by different functionals which are plotted in Fig. 4.13(b). The GGA+U with SOC exhibits a smooth increase in magnetic moment per unit cell In UX_3 series [216-217]. The lattice constant of UX_3 family far away from Hill limit it shows that there is strong hybridization present between the ligand s-, p- and d- orbitals. The antiferromagnetic structure is due to the overlapping of 5f- electrons with s-, p- and d- states.

Table 4.13: Calculated spin (μ_{spin}), orbital (μ_{orb}) and total magnetic moments ($\mu_{\text{tot}}=\mu_{\text{orb}}+\mu_{\text{spin}}$) in terms of Bohr magneton (μ_B) at U, In, Tl and Pb sites as well as per unit cell of UX_3 by different functionals with SOC.

Compounds	sites	Magnetic moment							
		GGA+U	HF-PBEsol	GGA+U+SOC			HF-PBEsol +SOC		
		μ_{spin}	μ_{spin}	μ_{spin}	μ_{Orb}	$ \mu_{\text{Tot}} $	μ_{spin}	μ_{Orb}	$ \mu_{\text{Tot}} $
UIn ₃	M ^{int}	0.2530	0.3150	0.2370	0.0000	0.0000	0.0340		
	M ^U	2.8210	2.2580	2.7750	-3.8650	1.0900	1.9540	-2.640	0.680
	M ^{In}	-0.0070	-0.0120	-0.0130	-0.0010	0.0130	-0.0120	-0.010	0.015
	M ^{In}	-0.0080	-0.0130	-0.0210	-0.0010	0.0210	-0.0170	-0.003	0.020
	M ^{Tot}	3.0590	2.6090	2.9660	-3.8660	0.8980	2.3330	-2.650	0.320
	U-U	4.6010							
Exp: μ_{B} /U16-17	1.0 ¹⁶⁻¹⁷								
UTl ₃	M ^{int}	0.2490	0.2780	0.1880	0.0000	0.0000	0.3230		
	M ^U	2.8280	2.3380	2.0480	-3.3140	1.3000	2.0690	-2.920	-0.85
	M ^{Tl}	-0.0030	0.0040	-0.0030	-0.0010	0.0030	-0.0070	-0.002	0.009
	M ^{Tl}	-0.0030	-0.0030	-0.0010	-0.0010	0.0010	-0.0070	-0.002	0.009
	M ^{Tot}	3.0700	2.6270	2.2420	-3.3150	1.0740	2.4100	-2.930	0.505
	U-U	4.6740							
Exp: μ_{B} /U	1.6 ¹⁶⁻¹⁷								
UPb ₃	M ^{int}	0.2180		0.2350			0.2060		
	M ^U	2.9390	2.7090	2.7000	-4.2590	1.5580	1.7710	-2.735	1.000
	M ^{Pb}	-0.0020	-0.0060	-0.0020	-0.0030	0.0050	-0.0050	-0.001	0.005
	M ^{Pb}	-0.0020	-0.0070	-0.0020	-0.0030	0.0050	-0.0040	-0.001	0.005
	M ^{Tot}	3.1540	2.8620	2.9320	-4.2640	1.3340	1.9630	-2.737	
	U-U	4.7920							
Exp: μ_{B} /U	1.70 ¹⁶⁻¹⁷								

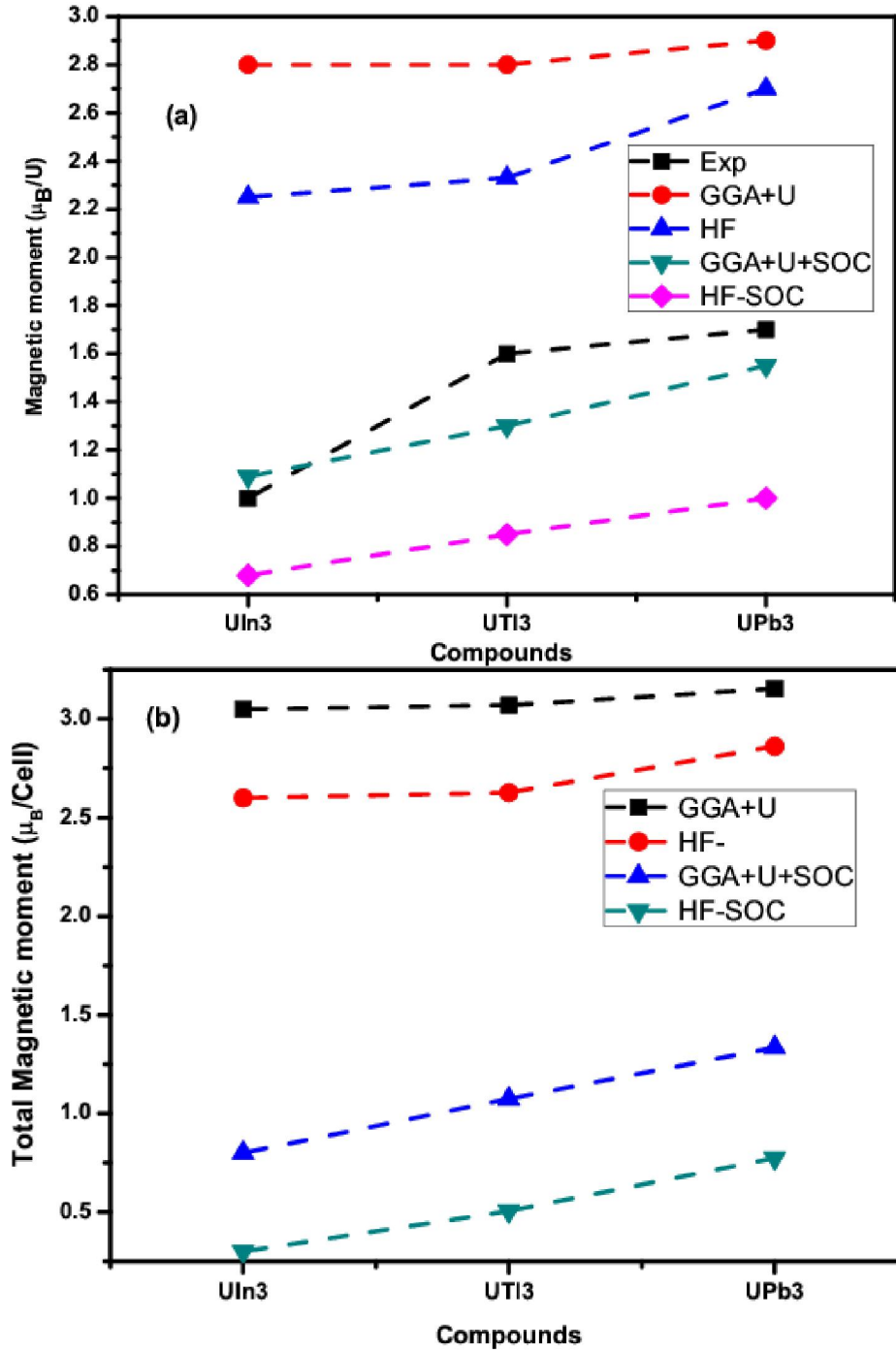


Figure 4.13: (a) The net magnetic moment in μ_B at uranium sites versus UIn₃, UTl₃ and UPb₃. (b) The computed entire magnetic moment μ_B per unit cell by using GGA+U, HF-PBEsol in absence and presence of SOC.

4.3.4 Hyperfine Field (HFF) and Electric Field Gradient (EFG) of UX_3 (X = In, Tl, Pb)

The nucleus site is not a mathematical point charge. The real nucleus is spherical or elliptical in nature. The nucleus has magnetic moment due to its non spherical nuclear charge distribution. The electronic cloud also produced an electronic magnetic dipole moment. These two fields interact with each other in the form of hyperfine interactions. Electric field gradient EFG is the rate of change of electric field produced by the electrons at the nucleus sites. The HFFs, EFGs and quadrupole coupling constant (Cq) are very important parameters which explain the distribution of electronic cloud around the nucleus and the bonding nature among electrons in molecules or atoms in condensed matter physics in biological materials [218]. The total HFF originate due to the orbital magnetic moment, spin magnetic moment of electrons as well as the neighboring atoms magnetic moments. The magnetic hyperfine field at the nuclear position due to orbital ($\vec{l}$) and spin angular momentum ($\vec{s}$) is;

$$H_{FF}^{tot} = 2\mu_B\gamma_\rho\hbar\vec{l}\left[\frac{\vec{l}}{r^3} - \frac{\vec{s}}{r^3} + 3\frac{(\vec{r}\cdot\vec{s})\vec{r}}{r^5} + \frac{8}{3}\pi\vec{s}\delta(\vec{r})\right] \quad 4.11$$

The first term in bracket stands for orbital moment of electrons, middle terms indicate the spin moments while the last term is the Fermi contact hyperfine interactions term [219]. Besides HFF EFG is also a vital factor which connect nuclear physics to condensed matter physics by formula ($C_Q = \frac{eQV_{zz}}{h}$). EFG is second rank tensor which predicts the charge distribution around the nucleus. The positive EFG shows oblate charge distributions while negative predict prolate distribution of electronic charge around the atomic sites. The principle component of EFG is V_{zz} where;

$$V_{zz} = \lim_{r \rightarrow 0} \left[\frac{5}{4\pi} \right]^{1/2} \left[\frac{V_{20}(r)}{r^2} \right] \quad 4.12$$

It is clear from equation (4.12) that the most important component of EFG tensor align to the z-axis, the other important parameter radial electric potential V_{20} , can be calculated as

$$V_{20}(r = 0) = \frac{4\pi}{5} \int_0^{R_{MT}} \frac{\rho_{20}}{r} dr - \frac{4\pi}{5} \int_0^{R_{MT}} \frac{\rho_{20}}{r} \left(\frac{r}{R_{MT}} \right)^5 dr \\ + 4\pi \sum_k V(k) J_2(kR_{MT}) Y_{20}(\hat{k}), \quad 4.13$$

where equation (4.13) consist of valence and lattice EFG. The first term of the equation (4.13) is contributed by the valence electrons of the atomic sphere while the other terms exhibit the contribution of lattice part of the atomic sphere. As the atomic sphere have three dimensional geometry, so $J_2(kR_{MT})$ specify Bessel function in spherical coordinate with radius R_M and the other term ρ_{20} show density of expansion with $L=2$ and $M=0$. The value of EFG for a single atom varies from materials to material. Therefore, many researchers considered EFG as the fingerprint for each compound [141,85,175]. EFG is one of the supportive parameter in investigation of electric quadrupole coupling constant (C_q) as well as the electric quadrupole interaction energy. EFG indirectly calculated from numerous experimental techniques like, NMR, NQR and Mössbauer spectroscopy [204].

In this thesis special concentration has been paid to investigate the orbital, dipolar, Fermi contact HFFs, EFG and C_q . We used different exchange correlation functionals in absence and presence of SOC calculations and find out the individual s-, p-, d- and f- orbital contribution in total HFF as well as EFG as shown in Table 4.14 and Table 4.15. The HFF due to spinning of electrons reach to the atomic site of uranium due to the spinning of p-, d- and f- state electrons are shown in Table 4.14 .The p- and f- orbital contributions to uranium sites due to dipolar

hyperfine is dominant whereas d- and p- take dominance in In, Tl and Pb atomic sites as exhibits in Fig 4.14 (a, b). The foremost dipolar HFFs value investigated in p- orbitals. The dipolar hyperfine values due to p- orbital in UIn_3 , UTl_3 and UPb_3 are 208.98 kGauss, 207.421 kGauss and 143.404 kGauss. There is an increasing trend in dipolar HFFs observed when one move from UIn_3 to UPb_3 . The dipolar HFFs of d- state electrons are also shown in Table 4.14. There is a decreasing trend in dipolar HFFs of d- orbital. The foremost contributions in total HFFs arise due to the orbital magnetic moment which behaves like a current carrying loop. The orbital contribution of partial HFF due to the post transition metals also investigated for the first as shown in Table 4.14. The major contributions arise due to the spinning of p- orbital, such that its magnetic effect diffused and reached to the atomic site as shown in Fig 4.14 (a, b). The orbital partial HFFs of UX_3 have been investigated by GGA and GGA+U, the p- and f- state electrons contribution is larger than other states. The dipolar, orbital, core and valence HFFs of UX_3 compounds are shown in Fig 4.15 (a,b). The dipolar and orbital HFFs are align at uranium sites which enhance the total HFFs. The Fermi contact HFF which is the sum of core and valence field of electrons has investigated by GGA with onsite Hubbard potential in the presence and absence of SOC. The valence and core electrons HFFs are opposite in direction due to the opposite magnetic moment of electrons. The Fermi contact HFFs increases from UIn_3 to UTl_3 and decreases from UTl_3 to UPb_3 as shown in Table 4.15.

The highest values of total HFF as well as Fermi contact field show the itinerant enature of electron density about the thallium sites, such fashion also examined by Ravindran *et al.* [85] for other elements. The total HFFs at In, Tl and Pb are very small due to the small magnetic moment of these elements in UX_3 series. The polarized f- state electrons and inner state electrons

interact to each other and contribute in core HFFs, while the local polarize f- electrons interact to the adjacent atoms and enhance the valence HFFs.

It is suggested that the cause of dipolar and orbital HFFs is the exchange interaction of f- and p- state electrons while d- and p- orbitals contributed in post transition metal in indium, thallium and lead sites. The negative magnetic moment of Uranium, Indium, Thallium and Indium cause the negative hyperfine field as shown in Table 4.14 and 4.15.

EFG is second rank tensor which can be computed directly by different theoretical approach as well as indirect experimental approaches. It helps in determination of nuclear electric quadrupole moment. The quadrupole coupling constant measured experimentally and principle component of EFG calculated computationally by using $C_Q = \frac{eQV_{zz}}{h}$. The quadrupole moment of the nuclei can be evaluated by matching computational and experimental values. The principal component of EFG at U, In, Tl and Pb has been investigated by GGA+U in presence and absence of SOC are shown in Table 4.15. The V_{zz} at Uranium site by GGA+U is - 2.6370 V/m², -2.533 V/m² and -1.74970 V/m². The calculated EFG at In, Tl and Pb sites are 12.0732 V/m², 35.8940 V/m² and 33.3543 V/m² by GGA+U. The SOC calculation slightly disturbed the EFG at uranium sites, the non significant effect has also observed by Diviset *et al.* [221] and Nourbakhsh *et al.* [222]. The V_{zz} values at post transition metals are 15.55 V/m², 36.5260 V/m² and 34.94 V/m² by using of GGA+U with SOC. The V_{zz} of post transition atoms are positive which predict the prolate type environment around the atomic sites. The asymmetry parameter (η) which measures the deviation of electrons from cylindrical symmetry of uranium as well as In, Tl and Pb site are calculated for the first time as shown in Table 4.15. The asymmetry parameter of Pb is larger than In and Tl which shows that Pb deviate more in UX₃ series. The EFG as well as η of the post transition metals are larger than uranium. The evaluated

η by GGA plus U is directly connected to the lattice constant which is in agreement with other available data [141,223]. The quadrupole coupling constant is an important parameter which shows strength of interaction energy between electric field of electrons and nuclear electric quadrupole moment. The quadrupole nuclei, ^{115}In , ^{204}Tl in addition to ^{207}Pb have nuclear electric quadrupole moment which are 0.73 barn, 0.74 barn and 0.34 barn [178, 278]. The quadrupole coupling constant of In, Tl and Pb are 288.00, 651.0 and 287.1 MHz, the corresponding quadrupole interaction energies are ≈ 1.19 , ≈ 2.7 and 1.19×10^{-8} eV. The C_Q and quadrupole interaction at uranium sites arise due to the 5f- and 6p- electrons while p-p and d-d exhibit dominance in UX_3 family. It has been suggested that C_Q as well as electric quadrupole interaction energies increase from top to bottom in column while decrease from left to right in periodic table, due to the varying electronegativity, volumetric effects and different states of orbital. The computed EFG at uranium site is helpful for experimentalist to evaluate the electric quadrupole moment of many nuclei like uranium which is a nuclear parameter and has several importances in nuclear physics. By using hyperfine interaction energy from NQR or NMR and use the $E_{HFF} = \mu HFF$ relation one can simply evaluate the magnetic moment of the nuclei. The electric quadrupole moment can be obtained by using $h\nu_Q = e^2 q Q$ formula. Therefore, EFG and HFF are the suggested values for experimentalist to measure nuclear magnetic moment at U, In, Tl as well as Pb sites and electric quadrupole moment of nuclei.

Table 4.14: The contribution of s-, p-, d- and f- states of dipolar and orbital HFFs at U, In, Tl and Pb sites by GGA and GGA plus U with SOC.

site		uranium site				x site (x = In, Tl, Pb)		
		S	p	D	f	s	p	d
dipolar GGA								
UIn ₃	up	0.00	-34.25700	-0.96100	-48.37100	0.00	27.81320	1.011300
	down	0.00	-174.7200	-01.1080	-11.83200	0.00	-20.95870	1.119200
	net	0.00	-208.9800	-2.07000	-60.20300	0.00	6.854500	0.108000
UTl ₃	up	0.00	-24.96580	-0.81230	-42.77200	0.00	68.17530	-3.083400
	down	0.00	-182.4550	-1.18950	-14.03600	0.00	-49.04330	3.3860 00
	net	0.00	-207.4210	-2.00170	-56.80800	0.00	19.13200	0.302600
UPb ₃	up	0.00	-32.11240	0.02910	-35.86860	0.00	65.92150	-1.423100
	down	0.00	-111.2910	-1.11300	-20.96940	0.00	-73.88090	1.764000
	net	0.00	-143.4040	-1.08380	-56.83800	0.00	-7.959400	0.340900
orbital GGA								
UIn ₃	up	0.00	-2105810	-69.8671	-1867.180	0.00	-34.57170	-19.93800
	down	0.00	2082980	42.1045	44.68630	0.00	32.11820	21.69610
	net	0.00	-2253.030	-27.7626	-1822.490	0.00	-2.453500	1.757700
UTl ₃	up	0.00	-2092340	-76.7110	-2023.170	0.00	-231.4200	-124.4440
	down	0.00	2068830	44.5180	9.693100	0.00	250.8650	127.3340
	net	0.00	-2350.910	-32.1930	-2013.480	0.00	19.44570	2.889800
UPb ₃	up	0.00	-2078040	-92.3229	-2033.140	0.00	-491.9780	-10.98930
	down	0.00	2054670	70.2845	101.6300	0.00	491.7640	11.39930
	net	0.00	-2337.000	-22.0384	-1931.510	0.00	-0.213800	0.410010
dipolar GGA+U								
UIn ₃	up	0.00	-3.161400	-0.08062	-3.966360	0.00	2.867120	-0.099500
	down	0.00	-18.29000	-0.12728	-1.253880	0.00	-2.114250	0.111200
	net	0.00	-21.45200	-0.20790	-5.220240	0.00	0.752870	0.011700
UTl ₃	up	0.00	-2.494900	-0.08122	-4.2770000	0.00	6.817680	-0.308330
	down	0.00	-18.24500	-0.11896	-1.403700	0.00	-4.904320	0.338600
	net	0.00	-20.74300	-0.20018	-5.680790	0.00	1.913360	0.030270
UPb ₃	up	0.00	-3.242980	0.00487	-3.564180	0.00	6.608630	-0.142260
	down	0.00	-11.3120	-0.11331	-2.092680	0.00	-7.400920	0.176770
	net	0.00	-14.55400	-0.10843	-5.656860	0.00	-0.792300	0.034500
orbital GGA+U								
UIn ₃	up	0.00	-21056.80	-6.94567	-185.1400	0.00	-3.281700	-2.013630
	down	0.00	20828.70	4.20255	4.575700	0.00	3.220650	2.170550
	net	0.00	-228.0800	-2.74313	-180.5600	0.00	-0.061000	0.156920
UTl ₃	up	0.00	-2092340	-76.7110	-2023.170	0.00	-232.2300	-126.7610
	down	0.00	2068830	44.5180	9.693100	0.00	254.6540	130.2340
	net	0.00	-2350.910	-32.1930	-2013.480	0.00	22.4240	3.473000
UPb ₃	up	0.00	-2078500	-9.32620	-212.5900	0.00	-49.72690	-11.01100
	down	0.00	20546.10	6.85019	5.301770	0.00	49.70880	11.34780
	net	0.00	-238.8000	-2.47610	-207.2800	0.00	-0.012040	0.330380

Table 4.15: The calculated total $|H_{hf}^{tot}|$, EFG, asymmetry parameter at U, In, Tl and Pb atomic sites in (kGauss) and V/m^2 by exchange-correlation functional GGA+U in absence and presence of SOC.

Potential	Site	$ H_{hf}^{tot} $	H_{hf}^{val}	H_{hf}^{cor}	H_{hf}^{dip}	H_{hf}^{orb}	EFG	ASYM	Q(barn)	
UIn ₃	U	4722.750	666.4240	-1014.660	-271.200	-4103.260	-2.63700	0.00		
	In	-136.9240	-142.8150	-0.376000	6.962500	-0.695800	12.07320	0.024		
UTl ₃	U	-5034.730	709.9010	-1081.900	-266.200	-4396.500	-2.53300	0.000		
	Tl	-251.0240	-291.6720	-1.127000	19.43460	22.34000	35.89400	0.004		
UPb ₃	U	-4401.070	605.3370	-913.9140	-201.320	-4290.500	-1.74970	0.000		
	Pb	-230.4240	-221.7600	-1.243000	-7.61850	0.197000	33.35430	0.009		
UIn ₃	U	-4800.390	669.4370	-1022.860	-268.800	-4114.000	-2.54800	0.000		
	In	-136.1880	-144.4600	-0.372000	7.700000	0.950000	15.55000	0.186	0.77	²¹⁶
UTl ₃	U	-5035.060	709.9020	-1081.920	-266.240	-4396.800	1.950000	0.000		
	Tl	-247.4610	-291.6600	-1.128 00	19.43000	25.89700	36.52600	0.189	0.74	²¹⁶
UPb ₃	U	-4998.770	607.2310	-916.3040	-203.200	-4486.500	0.692000	0.000		
	Pb	-227.5550	-221.8300	-1.328000	-7.57800	3.183000	34.94000	0.440	-0.34	²¹⁶ 52%

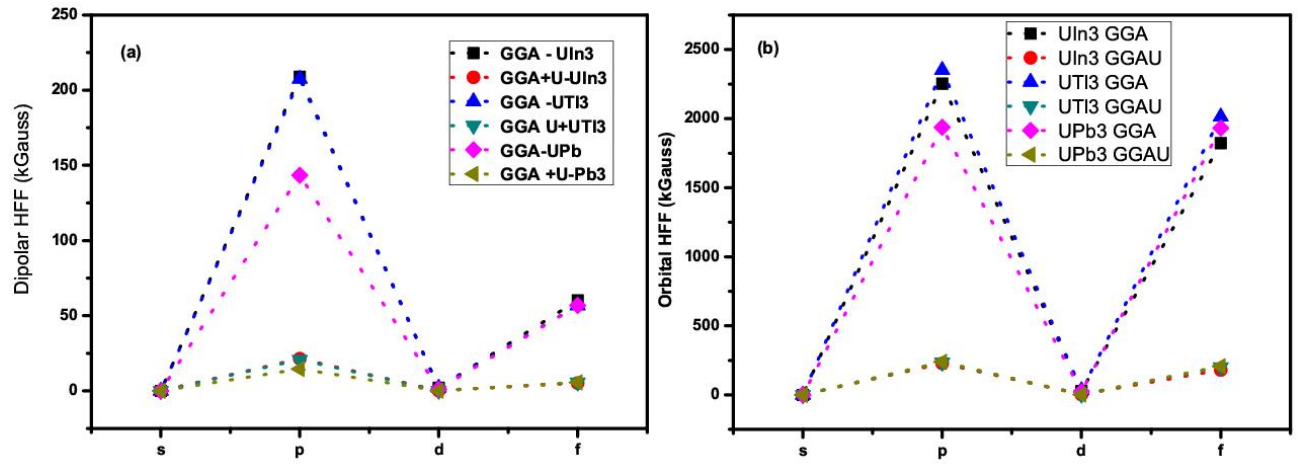


Figure 4.14. (a) Calculation of s-, p-, d- and f- state dipolar HFF in kGauss by different exchange correlation functionals. (b) Orbital HFF in kGauss versus contribution of each s- p-, d- and f- orbital.

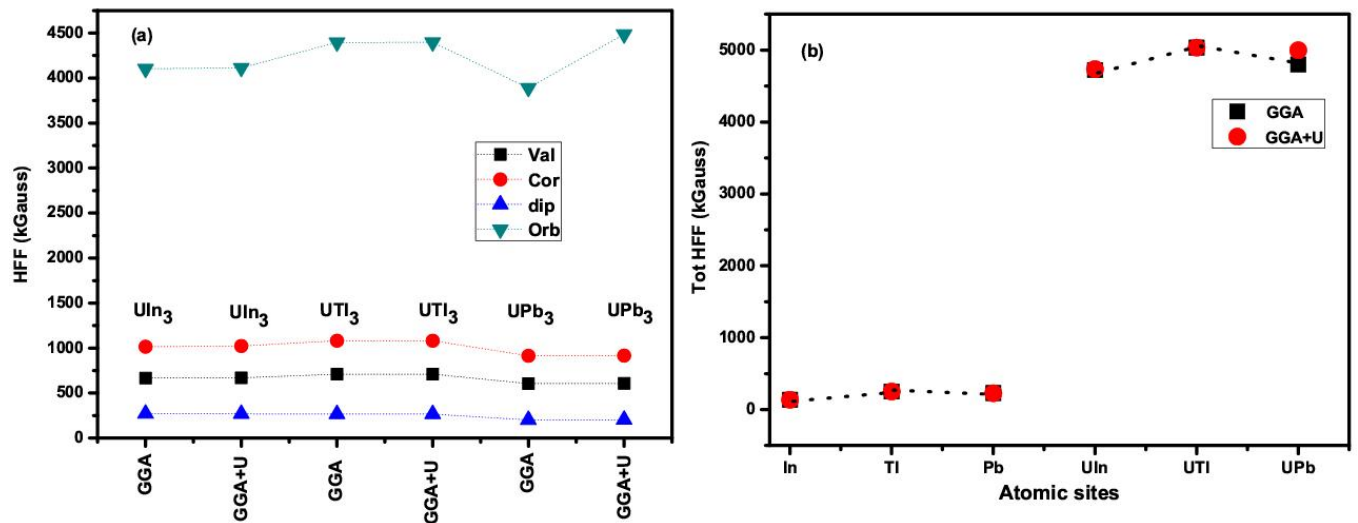


Figure 4.15: (a) Contribution of dipolar, orbital, core and valence HFFs of UX_3 by different exchange correlation functionals GGA and GGA+U with SOC. (b) Total HFFs at In, Tl and Pb sites in UX_3 .

Chapter 5

CONCLUSIONS

In this thesis full potential linearized augmented plane waves plus local orbital (FP-LAPW+lo) method within density functional theory (DFT) is used to explore the structural properties, like, ground state energy, lattice constants, bulk modulus and derivative of bulk modulus of AcGa_2 ($\text{Ac} = \text{U, Np, Pu}$), NpPX_3 ($\text{X} = \text{Al, Ga, In}$) as well as UX_3 ($\text{X} = \text{In, Tl, Pb}$) employing various exchange correlation functionals like LDA, GGA, LDA+U and GGA+U. It is observed that LDA, GGA, GGA+U and LDA+U can reproduce the experimental lattice parameters. The magnetic structure of these compounds has been checked in ferromagnetic, antiferromagnetic and non magnetic phases. The UGa_2 , NpGa_2 and NpPx_3 have lowest energies in ferromagnetic phase while PuGa_2 and UX_3 prefer in antiferromagnetic phase, which is in agreement with the experimental results.

These compounds have 5f- electrons and there is a strong interaction between angular momentum and magnetic moment, so to treat these appropriately we used SOC calculations. The magnetic moment, electronic specific heat, electric field gradient (EFG), hyperfine fields (HFFs) and quadrupole coupling constant of AcGa_2 , NpX_3 ($\text{X} = \text{In, Tl, Pb}$) and UX_3 ($\text{X} = \text{Al, Ga, In}$) compounds are calculated by LDA+U+SOC, GGA+U+SOC and HF+SOC. The spin and orbital magnetic moments are individually calculated and discussed in details. The calculated magnetic moment at uranium site is $0.88 \mu_B/\text{U}$, $1.3 \mu_B/\text{U}$ and $1.558 \mu_B/\text{U}$ in UX_3 compounds.

All the calculated magnetic moments at different actinide atomic site are consistent with experimental values. The electronic specific heat for NpAl_3 , NpGa_3 , NpIn_3 , NpUIn_3 , UTl_3 and UPb_3 has been calculated computationally for the first time using different exchange correlation

functionals. The hyperfine fields and its component orbital, dipolar and Fermi contact field as well as partial s- state, p- states, d- states and f- states has been investigated for U, Np, Pu and Ga in AcGa_2 and U, In, Tl and Pb sites in UX_3 compounds. It has been investigated that major contribution to HFFs arises due to the orbital hyperfine field in AcGa_2 and UX_3 .

The EFGs of the individual orbitals as well as C_Q of U, Np, Pu and Ga are investigated for the first time which shows the anisotropy of charges and interaction energy. It is concluded that the value of total EFG and HFFs at Ac site increases with the increase of atomic number from uranium to Pu. Our results also conclude the prolate distribution of electron at Ac site for all the considered compounds. It is also concluded that the C_Q value increases when one moves from Al to In in the NpPx_3 family. Uranium

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