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Theoretical studies of cubic $AuCu_3$-type intermetallic actinide compounds $NpPx_3$ (Px = Al, Ga, In)

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ABSTRACT

In this paper, we explore the structural, magnetic, electronic specific heat, electric field gradient (EFG) as well as quadrupole coupling constant of $NpPx_3$ (Px = Al, Ga, In) by using LDA, GGA, GGA + U and HF-PBEsol. The relativistic effects of electrons of the actinides are considered by spin-orbit coupling calculations. The comparison of the calculated structural parameters, magnetic moments and EFG of these materials satisfy the available experimental results. This consistency shows the effectiveness of our theoretical tools. The calculated EFG and quadrupole coupling constant value increase in $NpPx_3$ from Al to In due to change of fermions. The EFG and quadrupole coupling constant in $NpPx_3$ (Px = Al, Ga, In) is mainly originated from f-f and p-p contributions of Np atom and p-p contribution of Al, Ga and In atom.

1. Introduction

The actinide $NpPx_3$ compounds (Px = Al, Ga, In) crystallize in the $AuCu_3$ cubic type structure [1,2]. These compounds have 5f electrons. The 5f electrons show some remarkable physical properties like magnetic and electric hyperfine interactions, Pauli paramagnetism, large coefficient of electronic specific heat, heavy fermions, spin fluctuation and unconventional superconductivity in Condense Matter Physics [3–9]. The actinides and their intermetallic compounds are characterized by magnetic properties ranging from local moment behavior (rare-earth like) to itinerant, band-like character. This wide variety is mainly a consequence of the extra spatially extended nature of 5f-electrons compared to 3d- and 4f-electrons. H. H. Hill was the former to understand the crucial role of 5f-5f overlapping [10,11]. 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 only possible by the hybridization of 5f electrons with ligand orbitals [11]. Sanchez et al. experimentally studied the magnetic nature of $NpPx_3$ (Px = Al, Ga, In) compounds [12]. E. Colineau et al. studied $NpGa_3$ by 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 Tc ≈ 50 K, while Zwirner et al., observed experimentally that $NpGa_3$ is ferromagnetic under 50 K with magnetic moment 1.6 μ_B/Np [2,13]. J. 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 μ_B in $NpGa_3$ [13]. Dwight et al. concluded that $NpAl_3$ is ferromagnetic (T_C = 62.5 K) with a saturation moment of about 1.4 μ_B, while Oddou et al. demonstrated that $NpAl_3$ is a type II anti-ferromagnetic (T_N = 37 K) with a saturation moment of about 1.3 μ_B [14–19]. Large values of electronic specific heat of 100 and 72 $mJmol^{-1}K^{-2}$ are due to heavy fermions of neptunium atom have been experimentally measured for $NpGa_3$ and $NpIn_3$, respectively [20,21].

So far, to the best of our knowledge, no serious attention has been paid to the theoretical studies of $NpPx_3$ due to its heavy 5f electrons. In this study we explore 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

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Hubbard potential (GGA + U) and hybrid functional (HF-PBEsol) in the presence of spin polarized and spin-orbit coupling calculations.

2. Computational detail

We use full potential linearized augmented plane wave plus local orbital (APW + lo) method as implemented in WIEN2k code [22], which is based on density functional theory (DFT) within LDA [23,24], GGA (PBEsol) [25–28], GGA + U [29–31] and HF-PBEsol methods [32].

Density Functional Theory (DFT) is a computational method that calculates the ground state properties of many-body systems. It has some advantages and limitations. The most significant advantage to DFT methods is a significant increase in computational accuracy without the additional increase in computing time. DFT deals the exchange correlation energy in approximate way therefore when making comparisons with experiment one has to be careful to make the correct choice of exchange correlation functional.

It is well understood that local density approximation (LDA) and generalized gradient approximation functional of DFT gives a coincide result to the experimental one, especially for structure properties. These two schemes are cheap and are very sophisticated computationally. These functional have some limitations, which have been reduced with time. The foremost shortcoming of these approximations is that they have problems to describe the electronic structure of heavy fermions [8]. The significance of the heavy fermions and the limitations of LDA and GGA in these systems encourage researchers to think about new ideas and solution to such problem. To overcome such deficiency and for well treatment of heavy fermions LDA + U and GGA + U was introduced where U is the Hubbard parameter. However, this scheme has also some disadvantages, e.g., for applying this method, one needs to calculate U_{eff} (U-J) parameter. The determination of U_{eff} is time consuming and costly in experiment. In some cases the results of these approaches are not compatible to experimental results [23–31]. To treat heavy compounds like 4f and 3f Novak et al. introduced the HF− scheme or exact exchange for correlated electrons in 2006. This scheme gives very good result for heavy compound especially for magnetic properties [8,32]. Therefore, in order to get logical and acceptable theoretical results we are also using HF− in addition to other functional.

We calculate the structural, magnetic, electronic specific heat and electric field gradient (EFG) of $NpPx_3$ using the said potentials. The unit cell is divided into two parts non overlapping muffin-tin sphere of radii RMT and interstitial region. The Kohn–Sham (KS) [33] wave functions are expanded in terms of plane wave in interstitial region while spherical harmonic in muffin tin spheres. The electronic wave functions are arranged into two groups core electrons, which are localized within the atomic sphere and valence electrons with wave functions expand out of the MT spheres. The calculations were performed considering spin-orbit coupling (SOC) effects which are implemented in WIEN2k package [34,35]. The selected radii for $NpPx_3$ (Px = Al, Ga, In) compounds are R_{Np} = 2.7 a. u. and R_{Px} = 2.4 a. u. These are the optimized values which provide the stability of unit cell of the crystal in ground state. To give consistent results, a set of 126 k-points (12 × 12 × 12) in the irreducible wedge of the Brillouin zone was selected. The cutoff angular momentum quantum number value inside the muffin-tin sphere was confined to l_{max} = 10. The associated interstitial wave function were expanded in plane waves with a cutoff $K_{max} = 7/R_{MT}$ where RMT is the smallest MT radius in the unit cell. The charge density and the potential were Fourier expanded up to G_{max} = 12. These values were chosen for getting convergence charge and energy as well as lattice parameters.

3. Ground state structural properties

$NpPx_3$ [Px = Al, Ga, In] intermetallic compounds exhibit $AuCu_3$ type cubic crystal structures with space group Pm-3m (221), with atomic positions of Np 1(a); [0, 0, 0] and Px in 2(d) [0.5, 0.5, 0.0]; [0.0, 0.5, 0.5] and [0.5, 0.0, 0.5]. The experimental lattice constants of $NpAl_3$, $NpGa_3$ and $NpIn_3$ compounds are 4.269, 4.254 and 4.615 Å [2,36,37]. We have started from experimental lattice constant and relaxed the unit cell volume by minimizing the total energy versus unit cell volume and fitted the outcomes with a Birch-Murnaghan equation of state [38]. From the ground state volumes, the structural parameters like, lattice constants, bulk moduli, pressure derivatives, ground state energy and inter-distance of Np−Np and 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 1. 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. 1 (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. 2(a and 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 [36,39,40].

The bulk modulii are calculated by different exchange potentials as shown in Table 1. It is clear from Fig. 2 (b), that GGA (PBEsol) results are in agreement with the experimental results. It is suggested that GGA (PBEsol) calculation treat very well 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 $B^{/}$of bulk modulii which is an interesting parameter and have great physical significance in high pressure physics [41]. The magnetic nature of $NpPx_3$ has been checked by minimizing unit cell volume versus energy and concluded that these compounds have less

Table 1
Calculated ground state volume, lattice constant, bulk modulii (GPa), derivative of bulk modulii bond lengths of cubic $AuCu_3$ type $NpPx_3$ (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
$NpAl_3$				
Volume (Å)^3	77.80	75.00	77.20	
Lattice constant (Å)	4.269 [36]	4.212	4.257	
Bulk modulus (GPa)	74.00	94.60	73.32	73 ± 7 [36]
$B^{/}$		5.000	5.000	
E_{FM}			−118398.14	
E_{AFM}			−118398.05	
Np−Np (Å)			4.269	
Np−Al (Å)			3.01864	
$NpGa_3$				
Volume (Å)^3	76.50	71.40	74.00	
Lattice constant (Å)	4.246 [36] 4.254 [37]	4.149	4.192	
Bulk modulus (GPa)	97 [36] 75 [2]	104.7	96.30	96 ± 8 [36]
$B^{/}$	6.000 [2]	5.000	5.000	
E_{FM}			−138802.03	
E_{AFM}			−138801.94	
Np−Np (Å)			4.246	
Np−Ga (Å)			3.00238	
$NpIn_3$				
Volume (Å)^3	98.29	91.00	97.30	
Lattice constant (Å)	4.615 [36]	4.497	4.550	
Bulk modulus (GPa)	74.00 [36]	81.30	73.14	73 ± 2 [36]
$B^{/}$		5.000	5.000	
E_{FM}			−186057.55	
E_{AFM}			−186057.41	
Np−Np (Å)			4.615	
Np−In (Å)			3.263	

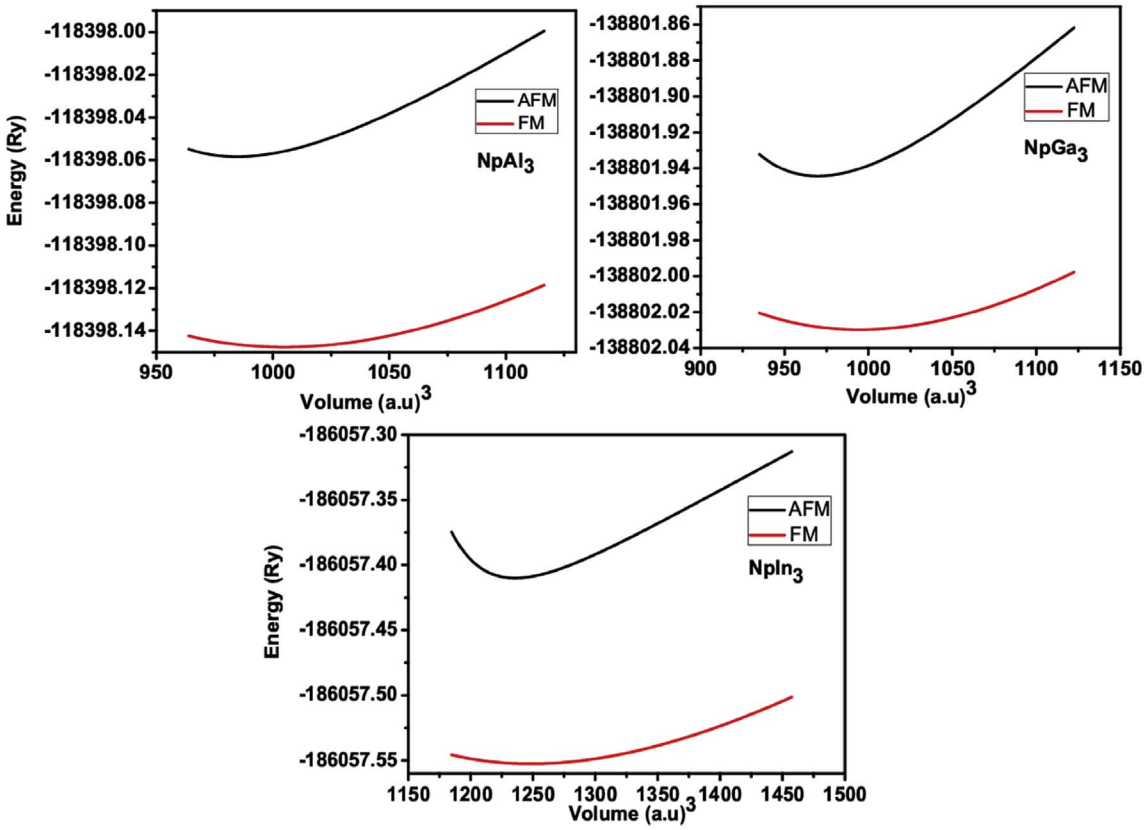

Fig. 1. (a, b, c). Variation of total energy versus unit cell volume of $NpPx_3$ (Px = Al, Ga, In). Under the GGA (PBEsol) functional.

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 1.

4. Magnetic nature of $NpPx_3$

The magnetic behavior of $NpPx_3$ [Px = 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) but the results are underestimated. This is due to well known self-interaction error (SIE) contained in LDA and GGA functional. 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. 3 (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 calculated values of spin, orbital and total magnetic moments for $NpPx_3$ by GGA-(PBEsol), GGA-(PBEsol) plus U and HF-(PBEsol) in addition to experimental results are shown in Table 2. The HF-PBEsol scheme gives the total magnetic moments of neptunium atom to be 1.6 μ_B/Np ($NpAl_3$), 1.64462 μ_B/Np ($NpGa_3$) and 1.59289 μ_B/

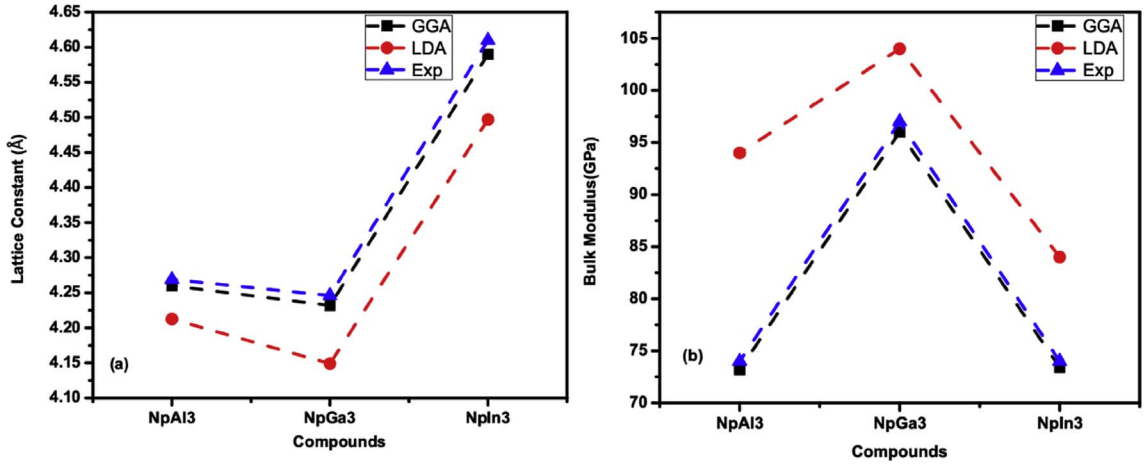

Fig. 2. (a, b). Experimental, LDA and GGA lattice constant as well as bulk modulii of cubic $NpPx_3$ (Px = Al, Ga, In) intermetallic compounds.

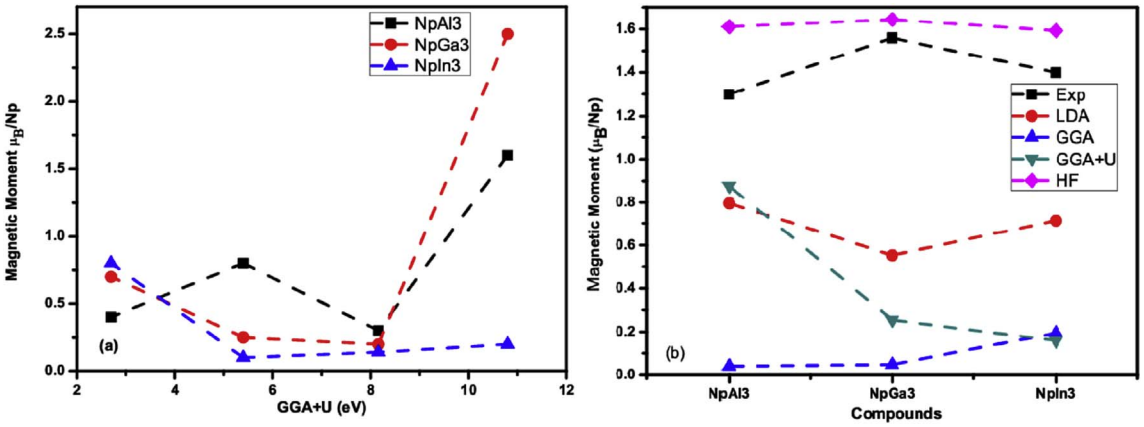

Fig. 3. (a, b). Calculate magnetic moment of $NpPx_3$ by using different values of U (b) Experimental as well as computational magnetic moment for $NpPx_3$ series.

Np ($NpIn_3$) which is consistent with the experimental results of J. L. Oddou, Sanchez et al. and E. Colineau et al. [16,42–44]. The HF-PBEsol with SOC improves the magnetic moment of Np, which means that hybrid function 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 (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 foremost contribution in spin magnetic moments originates from the non-spherical $5f^{+3}$ [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 1. In terms of *Hill limits* [11,45,46], it turns out that d (Np−Np) is remote from Hill limits ≈ 3.25Å 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 behavior of $NpPx_3$. It is clear from Table 2, that the orbital and spin magnetic moment ratio ($\mu l/\mu s$) almost remains constant for Np and Px by using different functionals.

5. Electronic and specific heat of $NpPx_3$ (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 $NpPx_3$ intermetallic compounds, we have calculated the total DOS in the absence and presence of spin-orbit coupling. In a conventional metal, the electronic specific heat is linked to the density of states at the Fermi level (E_F) through the following relation:

$$\gamma = \frac{\pi^2}{3} k_B^2 Dos(E_F) \tag{1}$$

where k_B is the *Boltzman's* constant and *Dos* (E_F) is the density of states at the Fermi energy [47]. 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 $NpPx_3$ are shown in Fig. 4 (a, b, c, d, e, f).

The results of calculated values of specific heat of electron are given in Table 3, by using HF-PBEsol in absence and presence of spin-orbit

Table 2
Calculated spin (μ_{spin}), orbital (μ_{orb}) and total magnetic moment ($\mu_{tot} = \mu_{orb} + \mu_{spin}$) in terms of Bohar magneton (μ_B) of $NpPx_3$ (Px = 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 [16]	62.5^F [16,44]
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		
μl/μs	1.2400	0.9800	1.2400	1.5600		
$NpGa_3$					1.56 [42]	4.2^F [42]
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		
μl/μs	1.1700	0.9800	0.9300	1.5700		
$NpIn_3$					1.4 [42]	10^F [42,43]
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		
μl/μs	1.2100	1.0600	0.9500	1.4700		

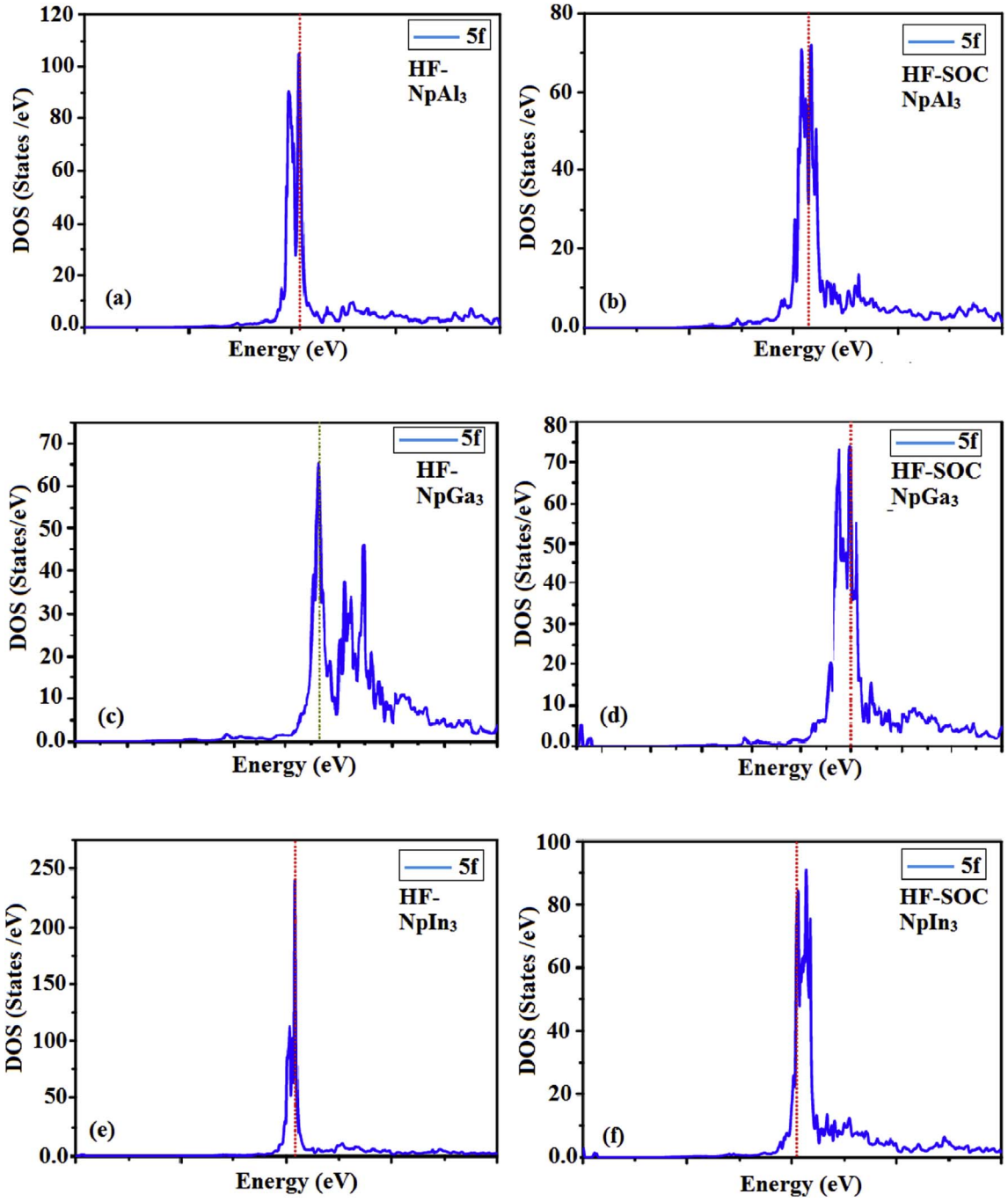

Fig. 4. (a, b, c, d, e, f). The density of states (a, b, c, d, e, f) with HF-PBEsol in absence and presence of SOC. The vertical dashed line indicates the Fermi level.

Table 3
The electronic specific heat (mJ mol^{-1} K^{-2}) in absence and presence of SOC of $NpPx_3$ (Px = Al, Ga, In).

	$NpAl_3$	$NpGa_3$	$NpIn_3$
Exp		100.0 [20]	72.00 [21]
HF-PBEsol	64.00	74.40	53.00
HF-PBEsol-SOC	78.20	85.00	62.00

coupling 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 [20,21]. The experimental electronic specific heat coefficient of atomic neptunium atom is 14.2 m J/mole K^2 [48]. The electronic specific heat coefficient of $NpPx_3$ (Px = Al, Ga, In) have been calculated computationally.

As shown in Fig. 4 (a, b, c, d, e, f), that f state cross the Fermi level this confirms the intermetallic nature of the $NpPx_3$. The specific heat major contributed by 5f-states electrons. The calculated γ values are 78.2, 85 and 62 mJ/mol K^2 for $NpPx_3$ (Px = Al, Ga, In) by using HF-PBEsol with SOC. As shown in Fig. 4, that valence band usually contributed by core electrons while conduction is due to unfilled d- and f-states electrons as well as d-and p states hybridization. The overlapping of valence and conduction band once again confirms the metallic as well as 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.

6. Electric field gradient (EFG)

Electric Field Gradient (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 [49–51]:

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

Equation (2) shows that major axis of EFG tensor points in the z-direction, where V_{20} is the radial potential and can be calculated as

$$V_{20}(r=0) = \frac{4\pi}{5}\int_0^{R_{MT}}\frac{\rho_{20}}{r}dr - \frac{4\pi}{5}\int_0^{R_{MT}}\frac{\rho_{20}}{r}\left(\frac{r}{R_{MT}}\right)^5 dr + 4\pi\sum_k V(k)J_2(kR_{MT})Y_{20}(\hat{k}), \quad (3)$$

Equation (3) has three terms; the first term shows the contribution of EFG due to valence or quasi-core in muffin-tin sphere. The second and third terms present the lattice contribution in EFG owing to the interstitial region, where ρ_{20} is the density expansion while $J_2(kR_{MT})$ is the spherical Bessel function in the Muffin-tin sphere. The value of EFG of a single atom is varying from compound to compound. 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 [52]. 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 Quadrupole Resonance (NQR), Nuclear Magnetic Resonance (NMR) and Mössbauer spectroscopy and High resolution techniques. The Quadrupole coupling interactions are routinely observed in NMR spectra in the form of line broadening [53,54]. It was found that the EFG provides a very sensitive probe of the anisotropy of the charge densities around the nuclei.

Major component of EFG cannot be measured by direct experiment, however if the nuclear electric quadrupole moment is known, V_{ZZ} can be obtained from C_Q. Otherwise, if V_{ZZ} computed from first principles, a plot of the experimental C_Q versus the calculated V_{ZZ} should be a straight line with a slope determined by eQ. This is a way to measure a nuclear quadrupole moment using a combination of experimental and computational tools.

Electric field gradient of actinide $NpPx_3$ (Px = Al, Ga, In) has been examined by using different potential 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 $NpPx_3$ (Px = Al, Ga, In) within different functional are tabulated in Table 4. 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 $NpPx_3$ (Px = Al, Ga, In) are small compared to incomplete d- and f–orbital contributions. In $NpPx_3$ (Px = Al, Ga, 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 1.1681×10^{21} V/m^2, 1.2276×10^{21} V/m^2 and 1.3234×10^{21} V/m^2 as shown in Table 4. The calculated values by different functionals are close to experimental value [2,16].

The Quadruple coupling constant ($C_Q = eV_{zz}Q/h$) [55] is a main parameter utilized for the purpose to calculate 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 [56]. The nuclear quadruple resonance (NQR) parameter, quadrupole coupling constants C_Q of $NpPx_3$ (Px = Al, Ga, In) has 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 Major contribution in NQCC is due to valence non-spherical $V_{zz}^{d\text{-}d}$ and $V_{zz}^{f\text{-}f}$ EFG. As shown in Fig. 5, the V_{zz}, CQ 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 energy 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, this increase is due to increase of p- orbital as well as different electronegativity from aluminum to indium.

7. Summary

In our study, different exchange potential like, LDA, GGA-(PBEsol), GGA + U and HF-(PBEsol) are used to investigate the nature of $NpPx_3$ (Px = Al, Ga, In) compounds. The ground state energy of these compounds is calculated which shows the ferromagnetic phase of these materials. The delocalization of these materials has been discussed under the Hill limit for actinide compounds. Our results of GGA (PBEsol) for structural properties are consistent to experimental results while HF-(PBEsol) calculated magnetic moments are appreciable. The specific heat as well as EFG of these materials has been discussed under different potential. The quadrupole coupling constant C_Q parameter and interaction energy have been calculated. The calculated C_Q value increases when one move from Al to In into $NpPx_3$ family. It is found

Table 4
Electric field gradient in 10^{21} × V/m^2, and NMR parameter coupling constant C_Q of intermetallic $NpPx_3$ (Px = Al, Ga, In) compounds by using GGA (PBEsol) and LDA in the presence of spin orbit coupling 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)
$NpAl_3$							
Np	1.0376	1.1681	1.13 [16]	105.64[16]	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
$NpGa_3$							
Np	1.1374	1.2276	1.59 [2]	148.86 [2]	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
$NpIn_3$							
Np	1.2980	1.3234	1.51 [16]	139.25 [16]	121	123	0.51
In	13.636	14.332	–	–	253	266	1.10
In	13.567	14.305	–	–	252	268	1.10

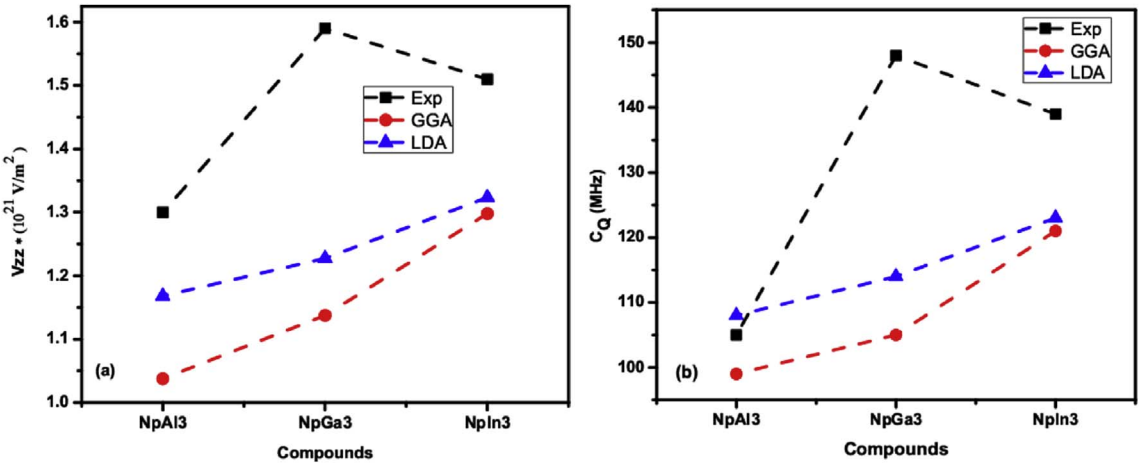

Fig. 5. (a). Calculated principle component of EFG for $NpPx_3$ (Px = Al, Ga, In) **(b)** and quadrupole coupling constant in MHz for $NpPx_3$.

that these parameters have great importance in NMR as well as NQR literature.

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