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First principles study on elastic properties and phase transition of NpN

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ABSTRACT

The mechanical properties of neptunium nitride (NpN) were investigated using first principles calculations based on density functional theory that take the Spin–Orbit Coupling (SOC) effect into consideration. With NaCl, CsCl and ZnS structures in nonmagnetic (NM), ferromagnetic (FM) and antiferromagnetic (AFM) states, the structure of NaCl in all magnetic states and that of ZnS, excluding the NM state without SOC, were found to be mechanically stable. The bulk moduli, elastic constants, Young's moduli, Poisson's ratios and anisotropic factors of NpN in stable states were also estimated. The enthalpies of NpN for NaCl and ZnS structures revealed that the phase transition of NpN from ZnS structure to NaCl structure took place at a pressure of −7.32 GPa, and hence the phase transition of NpN in a cubic system does not occur at positive pressure.

1. Introduction

Actinide nitrides are considered as promising advanced fuel materials for fast breeder reactors at the international Forum Generation-IV and as promising target materials for transmutation of minor actinides (MAs; Np, Am, Cm) using an Accelerator Driven System (ADS) due to their properties that include high metal density, high thermal conductivity, high melting point, mutual solubility of each nitride, and so on. Understanding the thermal properties of actinide nitrides is essential in validating the reprocessing feasibility of nuclear fuels cycles that involve the Partitioning and Transmutation (P & T) concept. However, few theoretical investigations of them have been reported to date. Fynn and Ray have reported on the electronic and magnetic structures and bulk moduli of AnN (An = Ac, Th, U, Np, Pu and Am) with the Spin–Orbit Coupling (SOC) effect taken into consideration [1]. Weck et al. have reported on the electronic structures and heat capacity of UN and UN_2 [2]. Sedmidubský et al. have reported on the formation enthalpy of AnN [3].

The elastic properties of neptunium nitride (NpN) were therefore focused on as they are connected to the lattice vibrations concerned with thermal properties. To our knowledge the elastic properties of NpN, such as elastic constants and the bulk modulus, have yet to reported on experimentally. Knowledge on the elastic constants enables us to realize the elastic and mechanical properties of the crystals. One of the goals of this paper was to clarify the elastic properties of NpN through evaluating its elastic constants, bulk modulus, shear modulus, Young's modulus and Poisson's ratio.

Nitrides have an almost rock salt (NaCl) structure in an ambient atmosphere. The phase transitions of lanthanum and gadolinium nitrides have been reported with regard to lanthanide nitrides. Lanthanum nitride (LaN) has been predicted theoretically to undergo a phase transition from NaCl structure to Cesium chloride (CsCl) structure at 26.9 GPa [4] and 25.25 GPa [5]. Contrastingly Zhao and Wu reported that LaN with CsCl structure is mechanically unstable because of the negative value of C_{44} [6]. It was also predicted that gadolinium nitride (GdN) would undergo a phase transition from Wurtzite structure to NaCl structure at −27.4 GPa and from NaCl structure to Zinc blende (ZnS) structure at 68.3 GPa [7]. However, no other phases have been reported on with regard to actinide nitrides, apart from α-$U_2N_{3+\delta}$ and β-U_2N_3 being identified experimentally with uranium nitride (UN). The other goal of this paper was to predict other stable phases of NpN and the phase transition from NaCl structure to another structures using first principles calculations.

2. Computational method

The elastic properties of UN, NpN and plutonium nitride (PuN) and phase transitions of NpN were calculated using Vienna Ab initio Simulation Package (VASP) code [8–11] within the Density Functional Theory (DFT) framework. The Projector Augmented Wave (PAW) [12,13] method within the Perdew–Burke–Ernzerhof (PBE) Generalized Gradient Approximation (GGA) [14] for the exchange–correlation functional was then applied. Scalar relativistic

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PAW potentials representing the core electrons of U (with $6s^26p^65f^26d^27s^2$ valence shell), Np (with $6s^26p^65f^46d^17s^2$ valence shell), Pu (with $6s^26p^65f^67s^2$ valence shell) and N($2s^22p^3$) atoms (containing 14, 15, 16 and 5 valence electrons, respectively) were used. In the calculations of the mechanical properties of actinide nitrides the SOC effect was considered to be important because f-electrons of actinide metals which should be solved have large angular momentum. A unit cell containing 8 atoms was used in the calculations. The plane-wave cut-off energy was set to be 500 eV for all structures in a cubic system. The Monkhorst–Pack scheme [15] for a $13 \times 13 \times 13$ *k*-point mesh in the Brillouin Zone was utilized for NaCl and ZnS structures and $17 \times 17 \times 17$ for CsCl structure. The total energy was converged to 1.0×10^{-5} eV/cell.

3. Results and discussion

3.1. Most stable structure of NpN

The total energy of the nonmagnetic (NM), ferromagnetic (FM) and antiferromagnetic (AFM) states with and without SOC were calculated in examining the most stable state of NpN. With the AFM and AFM–SOC states the type-I configuration was adapted because it has been reported that UN is an AFM state below 52 K [16] and has a type-I AFM configuration, as determined using a neutron diffraction measurement [17]. The total energies and energy differences relative to the ground state are listed in Table 1. First, it was clarified that the most stable state of NpN is ferromagnetic with and without SOC and then second that the total energy got lowered due to the SOC effect. This implied that the SOC effect would be an important factor in the actinide nitride calculations. Third, the most stable structure was revealed to be NaCl structure and the least stable CsCl structure. NaCl structure in a FM state with SOC was therefore regarded to be the ground state. These results agreed with an experimental report that NpN has NaCl structure in a ferromagnetic state below 83 K [18]. The equilibrium lattice constants of NpN for all the structures in all magnetic states are also listed in Table 1. The lattice constant had a good agreement with the experimental values with the ground states of 0.48956 nm [19], 0.48968 nm [20], 0.4897 nm [21], 0.48979 nm [18] and 0.48987 nm [22], with a below 1% discrepancy.

Table 1
Lattice constants a, total energies E_{tot} and energy differences ΔE from the ground state of NpN.

Structure	Magnetic	a (nm)	E_{tot} (eV)	ΔE (eV)
NaCl	NM	0.479	−23.007	4.010
	FM	0.488	−23.468	3.550
	AFM	0.487	−23.376	3.641
	NM–SOC	0.484	−26.796	0.222
	FM–SOC	0.487	−27.017	0
	AFM–SOC	0.487	−26.985	0.032
ZnS	NM	0.517	−21.914	4.741
	FM	0.524	−23.045	3.609
	AFM	0.528	−22.691	3.964
	NM–SOC	0.522	−26.099	0.556
	FM–SOC	0.525	−26.655	0
	AFM–SOC	0.528	−26.385	0.270
CsCl	NM	0.293	−21.465	4.193
	FM	0.299	−22.237	3.420
	AFM	0.298	−22.037	3.621
	NM–SOC	0.296	−25.197	0.461
	FM–SOC	0.299	−25.658	0
	AFM–SOC	0.299	−25.496	0.162

3.2. Elastic properties of NpN

The elastic properties of solids are closely related to many fundamental solid-state properties, including equation of states, specific heat thermal expansion, Debye temperature, Grüneisen parameter, melting point, and many others. The bulk moduli and elastic constants of NpN with NaCl, CsCl and ZnS structures in NM, FM and AFM states were evaluated. Twenty-one independent elastic constants were reduced to the three constants, C_{11}, C_{12} and C_{44} for use in a cubic system. The elastic constant of C_{11} represents the elasticity of length while C_{12} and C_{44} are related to elasticity of shape.

The bulk modulus and elastic constants of C_{11} and C_{44} were obtained through applying a small amount of strain, with a maximum value 0.5%, to the crystal. The bulk modulus was then calculated using the second-order differential of the total energy by volume. The elastic constants of C_{11} and C_{44} were also calculated using the second-order differential of the total energy by longitudinal strain and shear strain, respectively. The elastic constant of C_{12} can be related to the bulk modulus B and C_{11} using the following equation:

$$B = \frac{1}{3}(C_{11} + 2C_{12}). \tag{1}$$

The mechanical stability of each structure of NpN was then examined. To be considered stable elastic solids, Born stability criteria must be satisfied [23,24]. In a cubic system the stability criteria can be provided by the following relationships:

$$C_{11}, C_{44} > 0, \quad C_{11} - C_{12} > 0, \quad C_{11} + 2C_{12} > 0, \quad C_{12} < B < C_{11}. \tag{2}$$

It can be found that the computed bulk moduli and elastic constants NpN values satisfied the stability criteria provided by Eq. (2), apart from CsCl structure in all magnetic states and ZnS structure in a NM state without SOC. NpN with CsCl structure in all magnetic states was considered to be mechanically unstable because the elastic constant did not satisfy the criteria due to the negative value of C_{44}. NpN with ZnS structure in a NM state without SOC considered to be unstable because the elastic constants did not satisfy the criteria due to the relation of $C_{11} < C_{12}$. The obtained bulk moduli and elastic constants of NpN with NaCl and ZnS structures in mechanically stable states are listed in Table 2. The obtained bulk modulus for the ground state agreed with the value (183 GPa) calculated using WIEN2k code [1]. A difference in elastic properties appeared with the elastic constant of C_{11} especially. The elastic constant of C_{11} for NaCl structure was much larger than that for ZnS structure in all magnetic states. The elastic direction represented by the elastic constant of C_{11} is along the crystal axis. The direction of the bonding axis between Np and N atoms is equal to that of the elasticity of C_{11} in NaCl structure, although the direction deviates from that in ZnS structure. The elastic constant of C_{11} for NaCl structure is therefore considered to be larger than that for ZnS structure. Moreover, the SOC effect did not influence the elastic properties of NpN for NaCl and ZnS structures very much, although it did considerably influence the stability of NpN for each structure in terms of total energy. This then lead to the conclusion that the elastic properties much strongly depend on the crystal structures rather than magnetic states.

Once elastic the constants have been determined Young's modulus, shear modulus, Poisson's ratio and anisotropic factor can be evaluated using the Voigt–Reuss–Hill bounds [25,26], which are important elastic properties for applications. The Reuss bound represents the lower bounds for all lattices, while the Voigt bound represents the upper bounds for polycrystalline materials. The Voigt bulk modulus B_V and Reuss bulk modulus B_G are equal, with a

Table 2
Bulk modulus B and elastic constants C_{11}, C_{12}, C_{44} of NpN for stable states and of UN and PuN for NaCl structure in an AFM state with SOC with other theoretical values [1,28] and experimental data [29–31].

	Structure	Magnetic		B (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	Ref.
UN	NaCl	AFM–SOC		202	381	113	54.6	
			Other calc.	221				[1]
				203				[27]
			Expt.	206				[28]
				184				[29]
NpN	NaCl	NM		227	402	140	38.4	
		FM		147	331	54.2	79.1	
		AFM		179	341	97.7	60.8	
		NM–SOC		194	359	112	50.4	
		FM–SOC		168	330	86.4	60.7	
			Other calc.	183				[1]
		AFM–SOC		176	339	94.2	61.8	
	ZnS	FM		131	172	111	65.6	
		AFM		121	137	112	41.3	
		NM–SOC		129	136	125	61.0	
		FM–SOC		125	156	110	65.0	
		AFM–SOC		117	136	107	49.9	
PuN	NaCl	AFM–SOC		153	280	89.6	66.2	
			Other calc.	160				[1]

cubic system, and hence the bulk modulus is exactly $B_V = B_G = B$. The Voigt shear modulus G_V is given by:

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}), \tag{3}$$

and the Reuss shear modulus G_R is given by:

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{[3(C_{11} - C_{12}) + 4C_{44}]}. \tag{4}$$

Shear modulus G is therefore given by:

$$G = \frac{G_V + G_R}{2}. \tag{5}$$

Young's modulus E and Poisson's ratio v were calculated using the bulk modulus and the shear modulus provided by the above equations. These are then related to their moduli using the following equations:

$$E = \frac{9BG}{3B + G}, \tag{6}$$

and

$$v = \frac{3B - 2G}{[2(3B + G)]}. \tag{7}$$

With a cubic system anisotropic factor A can also be calculated from elastic constants using the following equation:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}. \tag{8}$$

It is known that micro-cracks in materials can be easily induced by significant elastic anisotropy, thus making evaluating anisotropic factors important in realizing their mechanical durability. With isotropic crystals the factor A is equal to 1, with any value larger or smaller than 1 indicating anisotropy. The magnitude of the deviation from 1 is the degree of elastic anisotropy of the crystal. Young's modulus, shear modulus, Poisson's ratio and anisotropic factor obtained for NpN for stable structures are listed in Table 3. Both NaCl and ZnS structures were anisotropic. Young's modulus for NaCl structure was larger than that for ZnS structure and Poisson's ratio for NaCl structure was smaller than that for ZnS structure in all magnetic states. Elastic properties such as Young's modulus and shear modulus and so on basically did not depend

Table 3
Voight, Reuss and averaged shear moduli G_V, G_R, G, the Young's modulus E, the Poisson's ratio v and the anisotropic factor A of NpN for stable states and of UN and PuN for NaCl structure in an AFM state with SOC with experimental data [28–30]. The Young's modulus in Ref. [29] is obtained with the sample of 93.1% theoretical density.

	Structure	Magnetic		G_V (GPa)	G_R (GPa)	G (GPa)	E (GPa)	v	A	Ref.
UN	NaCl	AFM–SOC		86.4	71.6	79.0	210	0.33	0.41	
						104	267	0.28		[28]
			Expt.			104	262	0.26		[29]
							201			[30]
NpN	NaCl	NM		75.5	53.5	64.5	177	0.37	0.29	
		FM		103	95.5	99.2	243	0.22	0.57	
		AFM		85.2	76.0	80.6	210	0.30	0.50	
		NM–SOC		79.5	65.9	72.7	194	0.33	0.41	
		FM–SOC		85.2	76.0	80.6	208	0.29	0.50	
	ZnS	FM		51.6	45.0	48.3	129	0.34	2.1	
		AFM		29.8	21.7	25.8	72.1	0.40	3.3	
		NM–SOC		38.8	12.1	25.4	71.6	0.41	11	
		FM–SOC		48.2	37.5	42.8	115	0.35	2.8	
		AFM–SOC		35.6	24.8	30.2	83.5	0.38	3.5	
PuN	NaCl	AFM–SOC		77.9	7505	76.7	197	0.29	0.69	

on magnetic state with and without SOC. The thermal properties of NpN are therefore considered to depend on crystal structure more than magnetic state.

3.3. Predicting of phase transition with NpN

The mechanical stability calculations indicated the possibility of structural phase transitions existing with NpN. The phase transition of NpN from NaCl structure to ZnS structure was therefore investigated. The phase transition induced by pressure occurs when the enthalpies of each structure are the same. Enthalpy can be represented by the equation of $H = E_{\mathrm{tot}} + PV$, where E_{tot} is total energy, P pressure and V unit cell volume. The total energies of NpN with NaCl and ZnS structures in a FM state with SOC are plotted in Figs. 1 and 2 as a function of volume, respectively. Pressure can be calculated as a volume derivative of total energy from interpolated total energy as a function of unit cell volume using:

$$P = -\frac{dE_{\mathrm{tot}}}{dV}. \tag{9}$$

The enthalpies for NaCl and ZnS structures are plotted in Fig. 3 as a function of pressure. As can be seen in Fig. 3 the phase transition from ZnS to NaCl structure took place at a pressure of −7.32 GPa. In other words NpN did not get transformed into any other structure in the cubic system under positive pressure. NpN underwent phase transitions more easily than other lanthanide nitrides such as LaN [4,5] and GdN [7] due to the absolute value of the phase transition pressure of NpN being smaller than the pressures of LaN and GdN. Moreover, a spontaneous jump in volume took place at the phase transition pressure, as revealed in Fig. 4. This appeared then to lead to the supposition that swelling occurs in nitride fuels during phase transitions due to discontinuity in volumes.

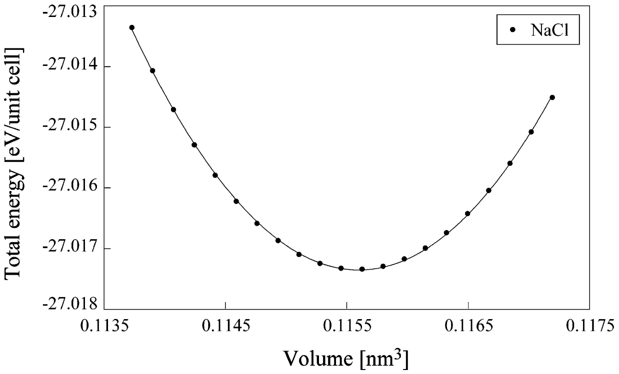

Fig. 1. Total energy of NpN for the ground state as a function of unit cell volume.

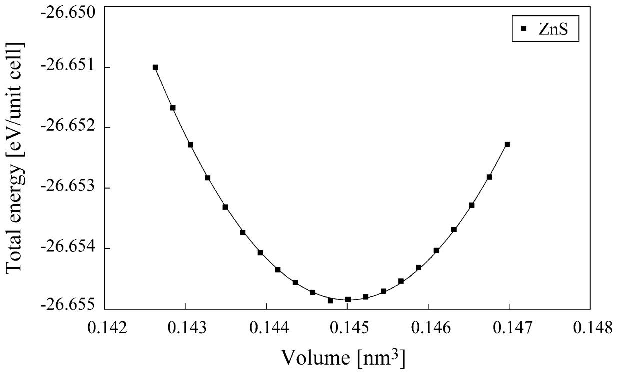

Fig. 2. Total energy of NpN for ZnS structure in a FM state with SOC as a function of unit cell volume.

3.4. Elastic constants of other actinide nitrides

Since the elastic properties of NpN could be clarified using first principles calculations the elastic properties of uranium and plutonium nitrides, which are also actinide nitrides, were examined in the same way. The AFM type-I configuration was adapted for the magnetic state of PuN because it was reported that PuN is an AFM state below 13 K [16]. The SOC effect was also taken into account in the of UN and PuN calculations. The obtained bulk moduli, elastic constants, Young's moduli, shear moduli, Poisson's ratios and anisotropic factors of UN and PuN in an AFM state with SOC are listed in Tables 2 and 3, along with other theoretical values [1,27], and experimental data reported on UN [28–30]. The calculated bulk modulus agreed fairly well with the experimental data. After taking into consideration the calculated and other theoretical values of the bulk modulus, the error included in the elastic properties, for example the bulk modulus and elastic constants, obtained in the first principles calculations was regarded as being about 10%. Among UN, NpN and PuN bulk moduli were small with large lattice constants as the atomic number of the actinide metals was large, thus implying that bonding strength increases as the atomic number decreases. However, the number of valence electrons increased with increasing atomic number. These results led to the conclusion that the valence electrons do not broaden but re-

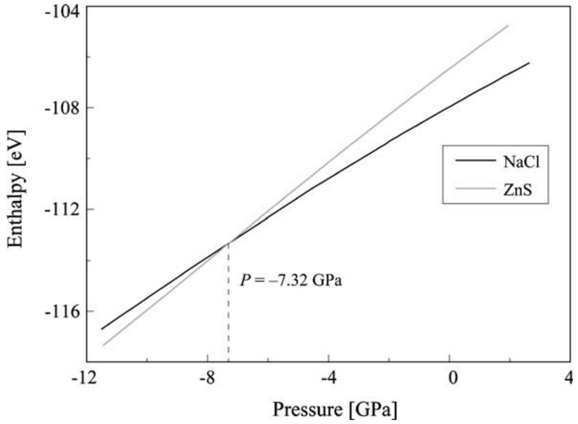

Fig. 3. Enthalpies of NpN for NaCl and ZnS structures as a function of pressure.

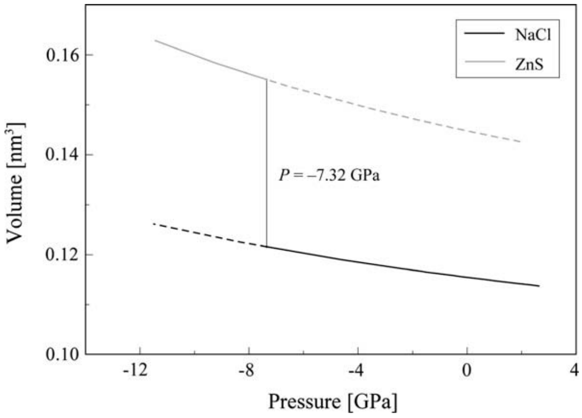

Fig. 4. Volumes variation of NpN for NaCl and ZnS structures as a function of pressure.

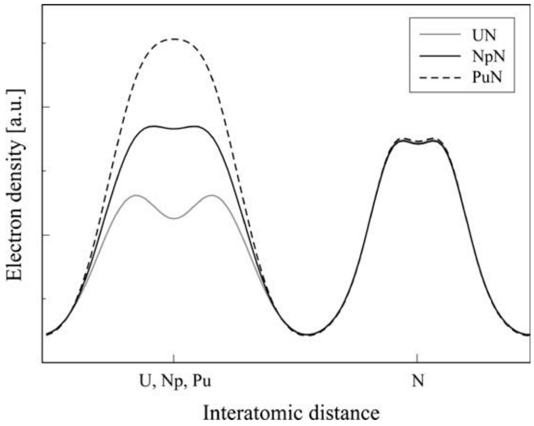

Fig. 5. Electron densities of UN, NpN and PuN along the bond axis between actinide and nitrogen atoms.

main localized around the atoms. To validate this conclusion, the electron densities of UN, NpN and PuN in the ground state are plotted in Fig. 5. The interatomic distance between actinide and nitrogen atoms was normalized in the figure. Electron densities varied at the center of the actinide atoms whereas they were basically the same between actinide and nitrogen atoms and at the center of the nitrogen atom.

With UN the calculated Young's modulus and shear modulus were underestimated and the calculated Poisson's ratio overestimated when compared to the experimental values. The differences, those beyond the theoretical error, were believed to be attributable to the UN sample conditions. The samples contained impurities such as oxygen and carbon to a certain extent. Anisotropy appeared in UN the most strongly of UN, NpN and PuN. Zirconium nitride (ZrN) [31] and titanium nitride (TiN) [32], candidates for use in the inert matrix of nitride fuels, are also anisotropic, although LaN [5] is isotropic rather than anisotropic.

4. Conclusions

The mechanical properties of NpN were evaluated with NaCl, CsCl and ZnS structures in NM, FM and AFM states with and without SOC by means of first principles calculations based on DFT. The SOC effect was considered very important in calculating the total energy of actinide nitrides. The equilibrium lattice constant of NpN for the ground state agreed well with experimental values with a discrepancy of below 1%. The elastic constants of NpN for CsCl structure in all states and for ZnS structure in a NM state without SOC were found to be mechanically unstable. The calculated bulk modulus of NpN for the ground state agreed with the other calculated value. Differences in the crystal structure appeared with the elastic constants of C_{11} especially. It was considered that the thermal properties of NpN depend more on the crystal structure than on quantum effects such as the SOC and magnetic state. NpN was also found to be an anisotropic material. The phase transition of NpN from NaCl structure to other structures was investigated through estimating enthalpy for NaCl and ZnS structures. The phase transition from ZnS structure to NaCl structure occurred at a pressure of -7.32 GPa, revealing that NpN with NaCl structure does not undergo any phase transition to another structure under positive pressure.

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