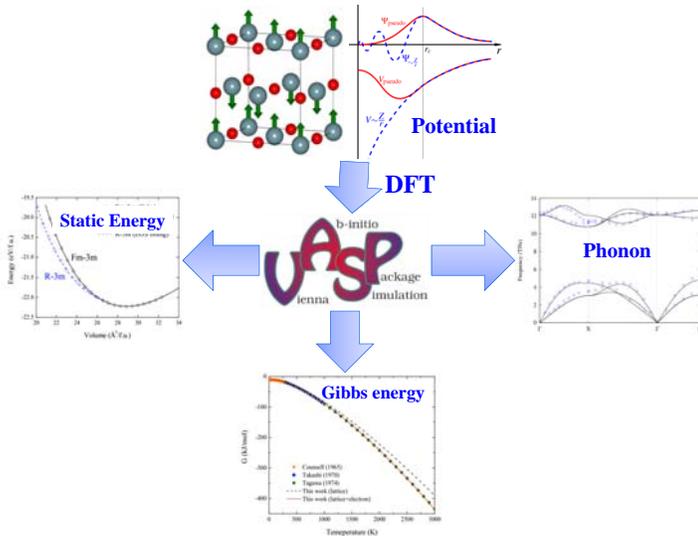


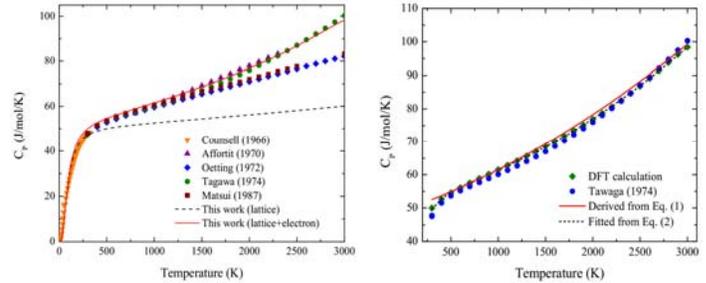
Uranium nitride (UN) is a promising fuel for the future fast neutron reactors due the superior thermophysical properties compared with the traditional oxide fuels. The thermodynamic properties and phase stability of UN determine the fuel performance and impact the reactor safety. In this work, we perform a systematic study of the thermodynamic properties and phase stability of UN, using density-functional theory (DFT).

Computational Methodology

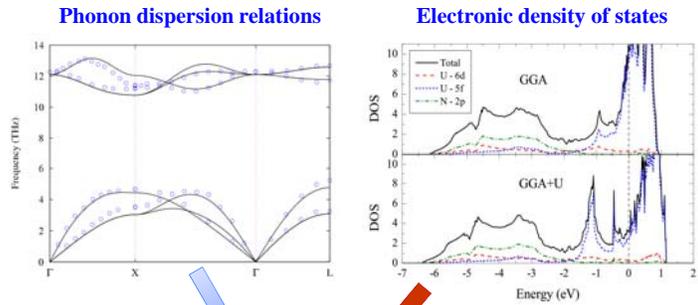


Specific heat at constant pressure (C_p) is estimated by two models:

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P \quad (1) \quad C_p = C_v + \alpha^2 V B T = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V + \alpha^2 V B T \quad (2)$$

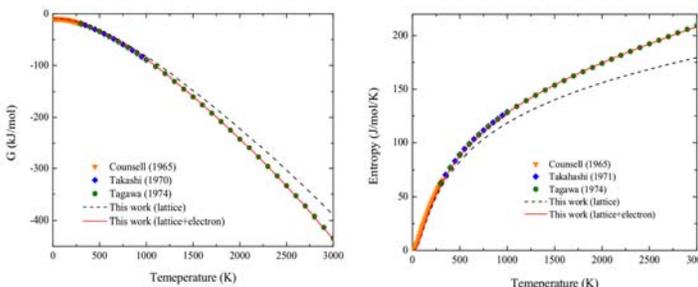


First-principles Thermodynamics



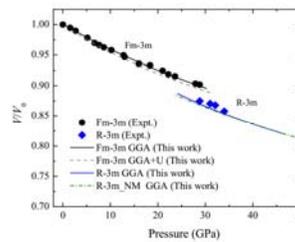
$$G(P, T) = E_0(V) + F_{\text{vib}}(V, T) + F_{\text{el}}(V, T) + PV$$

E_0 : 0K static energy
 F_{vib} : Lattice vibrational free energy
 F_{el} : Thermal electronic free energy
 PV : PV work

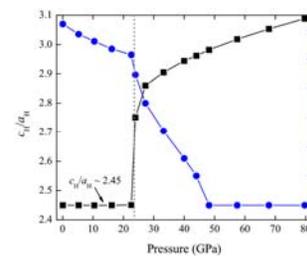


Due to metallic character of UN, the thermal electronic contribution to the free energy at high-temperature must be included. The thermodynamic properties of UN predicted by DFT method are in excellent agreement with experimental data.

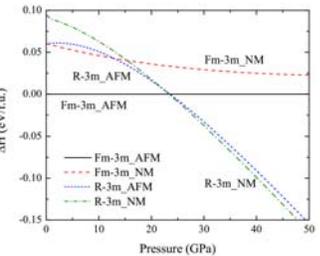
Pressure-induced Phase transitions



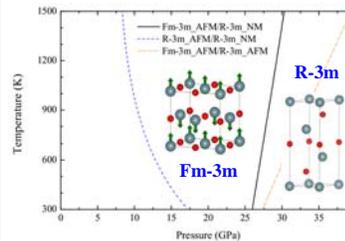
The pressure-volume relations of UN are studied by both GGA and GGA+U approaches. Our calculations show that GGA can describe the high-pressure behavior of UN very well.



The calculated lattice parameters and magnetic moment of the rhombohedral phase of UN indicate pressure-induced isostructural and magnetic transitions at increasing pressures.



The pressure-induced phase transitions of UN were also predicted from the calculated enthalpy agrees



From the calculated Gibbs free energy, the two-phase equilibrium line between AFM Fm-3m and NM R-3m phases of UN was predicted. The phase boundary can be described by a linear relationship between T and P . The metastable phase boundaries of UN were also provided.

Conclusions

- Thermal electronic contributions must be included in DFT calculations of thermodynamic properties of UN.
- The DFT-predicted pressure-induced isostructural and AFM to NM phase transitions in the rhombohedral phase of UN occur at 22 GPa and 48 GPa, respectively.
- The DFT equilibrium pressure-temperature phase diagram of UN shows a linear Fm-3m/R-3m phase boundary.