Phase stability of actinide carbides

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Introduction

What do we do?

- prospective nuclear fuels for IV. generation nuclear reactors
- calculating materials properties using quantum mechanical calculations
  - experimental research too expensive

What are we interested in?

- 5f-electrons behavior
  - not localized but itinerant, especially at high temperatures
  - possible study of other 5f compounds
- nuclear fuels
  - heat capacity, thermal conductivity

Goals

Motivation

- there was only one study[1] that calculated energy − volume curves and elastic constants of U_2C_3
- No Th_2C_3 in phase diagram of thorium carbides
  - Krupka[2] managed to sythesize Th_2C_3 only under high pressure

Questions

- What is the magnetic order of our compounds?
- What is the effect of spin-orbital coupling?
- What is the electronic structure of the phases?
- Is Th_2C_3 stable at ambient pressure?
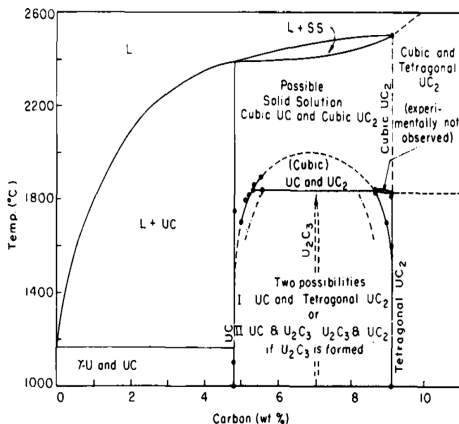- What is the best way to model properties of selected structures?

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[1] H. Shi et al., J. Nucl. Mater., 396, 218-222 (2010).

[2] M. C. Krupka, J. Less-Common Metals 20, 135-140 (1970).

Uranium Sesquicarbide

Available experimental data

- Cubic, space group 220 (I-43d), Pu_2C_3 type[1]
- Lattice parameter[1,2], density[3,4], $C - C$ bond length[5,6]
- Thermal conductivity[4] for $T = 1000 - 2200\,K$
- Thermal expansion[7,8] for $T = 1300 - 2000\,K$
- Thermodynamic properties (e. g. heat capacity[8,9] for $0 - 330\,K$)

[1] W. B. Wilson, J. Am. Ceram. Soc., 43, 77-81 (1960).

[2] J. F. A. Hennecke and C. J. Toussaint, J. Appl. Crystallogr. 2, 301 (1969).

[3] M. W. Mallett et al., J. Electrochem. Soc. 98, 12 1961., [4] R. De Coninck et al., J. Nucl. Mater., 46, 213-216 (1973).

[5] A. E. Austin, Acta Cryst., 12, 159-161 (1959)., [6] H. Shi et al., J. Nucl. Mater., 396, 218-222 (2010).

[7] R. De Coninck et al., J. Nucl. Mater., 46, 213-216 (1973)., [8] R. J. L. Andon et al., Trans. Faraday Soc., 60, 1030-1037 (1964).

[9] J. M. Leitnaker and T. G. Godfrey, J. Nucl. Mater., 21, 175-189 (1967).

Methodology

- Born-Oppenheimer approximation
  - calculations include only electrons, not atomic cores
- we calculate electron density[1], not electron wavefunctions
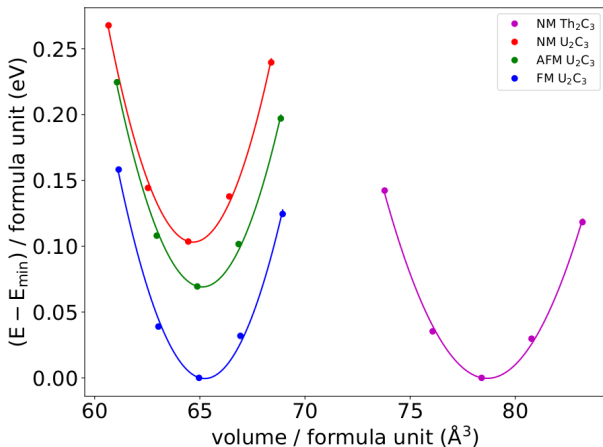- SCF - Self-Consistent Field
  - iterative method

Density Functional Theory (DFT)

- potential of all particles can be rewritten as electron density[1]
- Kohn-Sham orbitals[2] - orbitals close to real ones
  - one electron in the field of other electrons
  - variation principle - there is only one density that corresponds to global energy minimum

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[1]Hohenberg, P. and Kohn, W., Phys. Rev. B, 136, *B*864–& (1964).
[2]Kohn, W. and Sham, LJ, Phys. Rev., 140, 1133–& (1965).

Results - Ground-State Properties

U_2C_3	$a[\text{Å}]$
our work	8.1061
exp.[1]	8.0870
exp.[2]	8.0899
theory[3]	8.0970

Th_2C_3	$a[\text{Å}]$
our work	8.5599
exp.[4]	8.5555

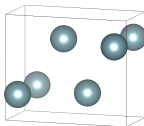[1] W. B. Wilson, J. Am. Ceram. Soc., 43, 77-81 (1960).

[2] J. F. A. Hennecke and C. J. Toussaint, J. Appl. Crystallogr. 2, 301 (1969).

[3] H. Shi et al., J. Nucl. Mater., 396, 218-222 (2010).
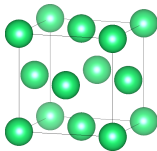
[4] M. C. Krupka, J. Less-Common Metals 20, 135-140 (1970).

Results - Enthalpy of Formation

	$\frac{\Delta H_f}{\text{formula unit}}$ [eV]
NM U_2C_3	-1.037
AFM U_2C_3	-1.060
FM U_2C_3	-1.127
FM+SOI+U U_2C_3	-1.428
NM Th_2C_3	-1.706

$$\Delta H_f = E_{Ac_2C_3} - (2\,E_{Ac} + 3\,E_C)$$

Thorium - Cubic (fcc)
Space group: 225 (Fm-3m)
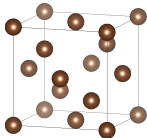Wyck.: 4a   exp[2].:
a = 5.0408 Å a = 5.180 Å

Uranium - Orthorhombic
Space group: 63 (Cmcm)
Wyck.: 4c   exp[1].:
a = 2.8087 Å a = 2.854 Å
b = 5.8379 Å b = 5.870 Å
c = 4.9160 Å c = 4.955 Å

Carbon - Cubic (diamond)
Space group: 227 (Fd-3m)
Wyck.: 8a   exp[3].:
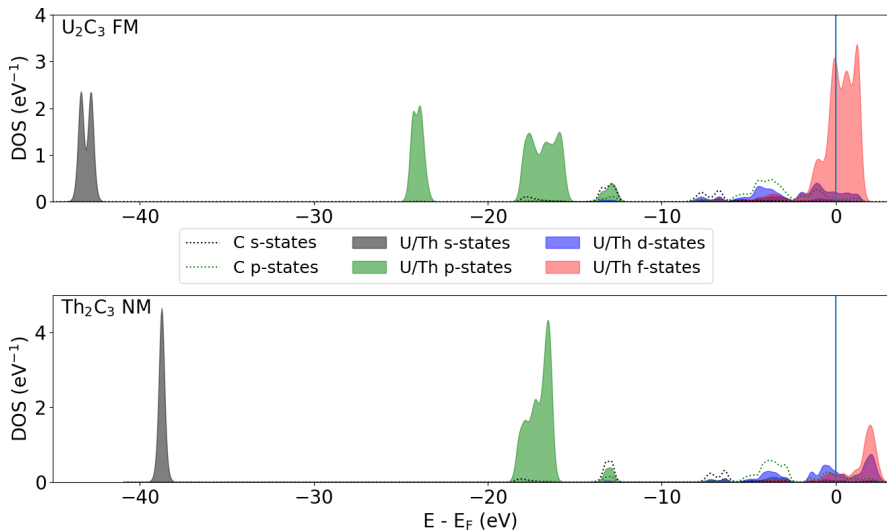a = 3.5716 Å a = 3.5597 Å

- Both U_2C_3 and Th_2C_3 are stable at $0\,\text{K}$ and ambient pressure

- U_2C_3 is ferromagnetic while magnetism plays no role in Th_2C_3's enthalpy of formation

[1] I. Grenthe et al., *The Chemistry of the Actinide and Transactinide Elements* (Springer, Dordrecht, 2008).

[2] Premo Chiotti, J. Electrochem. Soc. 110, 567-570 (1954).

[3] M. E. Straumanis and E. Z. Aka, J. Am. Chem. Soc. 73, 5643-5646 (1951).

Results - Density of States

Mechanical Properties

- for a cubic system, there are three independent elastic constants[1]

$$C_{cubic} = \begin{vmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ & c_{11} & c_{12} & 0 & 0 & 0 \\ & & c_{11} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{44} & 0 \\ & & & & & c_{44} \end{vmatrix}$$

- Young's modulus[1] - materials resistance to uniaxial deformation
  - $E = \frac{(c_{11}-c_{12})(c_{11}+2c_{12})}{c_{11}+c_{12}}$
- Shear modulus[1] - materials resistance to shear stress
  - $G = c_{44}$
- Bulk modulus[1] - materials resistance to compression
  - $B = \frac{c_{11}+2c_{12}}{3}$

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[1] G. Grimvall, *Thermophysical Properties of Materials* (Elsevier, North-Holland, Amsterdam, 1999).

Results - Mechanical Properties

- Born's elastic stability conditions[1] for cubic system
  - $(c_{11} > |c_{12}|) \wedge (c_{44} > 0)$
- Pugh ratio[2] $\frac{G}{B}$ - brittle to ductile border at 0.57
- Zener anisotropy[1] A_Z - if equal to 1, the material is isotropic
  - $A_Z = \frac{c_{44}}{C'} = \frac{2c_{44}}{c_{11} - c_{12}}$
- Poisson's ratio[1] - brittle to ductile border at 0.26
  - $\nu = \frac{3B - 2G}{2(3B + G)}$

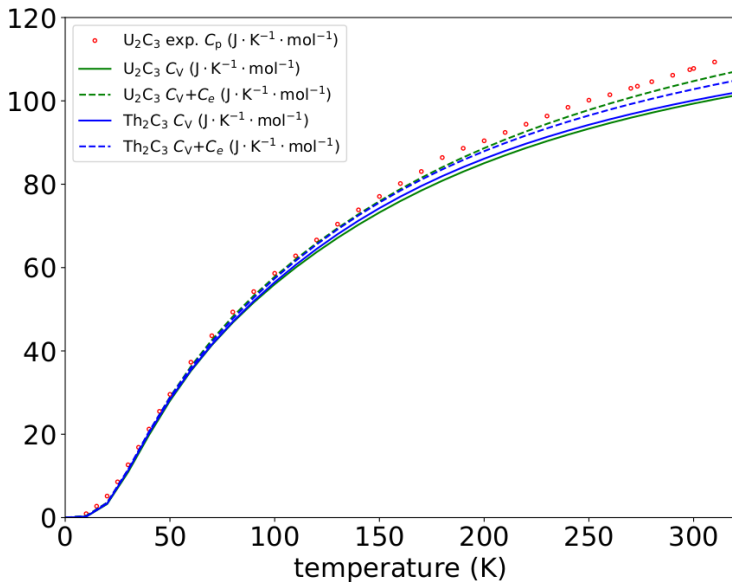| GPa	c_{11}	c_{12}	c_{44}	B	E	G	$\frac{G}{B}$	A_Z	ν
Th_2C_3	310	96	84	167	234	92	0.55	0.79	0.27
U_2C_3	311	129	101	189	249	97	0.51	1.11	0.28
Shi et al.[3]	383	121	91	208	238[4]	91[4]	0.44[4]	0.69[4]	0.31[4]

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[1] G. Grimvall, *Thermophysical Properties of Materials* (Elsevier, North-Holland, Amsterdam, 1999).

[2] S. F. Pugh, Philos. Mag., 45, 823-843 , (1954).

[3] H. Shi et al., J. Nucl. Mater., 396, 218-222 (2010).

[4] For a cubic system, $G \approx c_{44}$; we calculated marked values using this fact

Discussion

Conclusion

- U_2C_3 is FM with about 0.07 eV/f.u. lower than AFM ordering
- Th_2C_3 is non-magnetic and stable at 0 K and ambient pressure
- magnetism in U_2C_3 originates from the $\approx 7\times$ more $5f$ electrons than in Th_2C_3
- the chemical bonding in U_2C_3 and Th_2C_3 is caused by $5f$ and $6d$ electrons, respectively
- both phases are anisotropic and lie on the verge of brittle-to-ductile behavior, with U_2C_3 being slightly more ductile
  - U_2C_3: $\frac{G}{B} = 0.51$
  - Th_2C_3: $\frac{G}{B} = 0.55$
- calculated temperature dependence of heat capacity with its electronic contribution is in a good agreement with experimental values

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[1] H. Shi et al., J. Nucl. Mater., 396, 218-222 (2010).