High-precision predictions of properties of chemically disordered crystals

Nikolai A. Zarkevich[1], Timothy M. Smith[2], John W. Lawson[1]

[1] NASA Ames Research Center, Moffett Field, California 94035, USA

[2] NASA Glenn Research Center, Cleveland, Ohio 44135, USA

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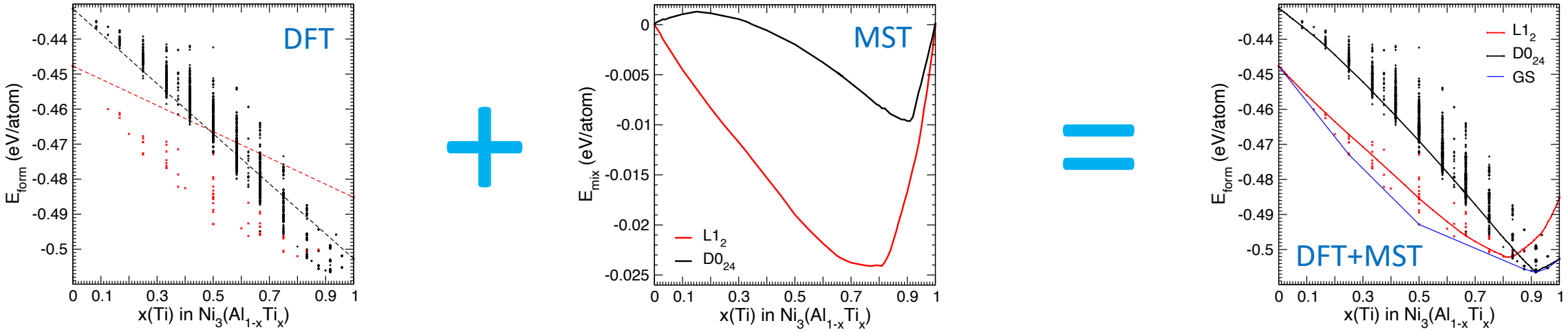

Outline

- Multiple scattering theory (MST) combined with density functional theory (DFT) allows to predict properties of chemically disordered materials from the first principles.
- Such predictions suffer from the systematic errors, which depend on crystal geometry. Each computed property of a particular crystal structure typically has a relatively small random error and a larger systematic error.
- Cancellation of systematic errors allows more accurate predictions. We propose a computational methodology based on the subtraction of the systematic errors in MST.
- To exemplify it, we apply it to the precipitated alloys. Considering precipitation strengthening in Ni superalloys, we compute the relative enthalpies of the competing $Ni_3(Al,Ti)_1$ crystal structures with a chemical disorder on the Al+Ti sublattice.
- Such predicted composition-structure-property dependencies are useful for the guided design of the next-generation alloys with improved strength. Our predictions are validated by comparison with the results of other DFT methods and with experiment.

Subtraction of systematic errors

- Approximation = Exact + Error

$$X_i = X_0 + \varepsilon_i$$

- X_0 is the exact value; X_i are approximations; ε_i are errors; $\varepsilon_1 < \varepsilon_2$.

  $X_1 = X_0 + \varepsilon_1 = (X_0 + \varepsilon_2) + (\varepsilon_1 - \varepsilon_2) = X_2 + (X_1 - X_2)$.

- Assume slow (rapid) variation of systematic (random) error; random errors can be small compared to systematic errors.

- If 2 approximations differ in accuracy, then systematic error can be reduced to that of the higher-accuracy approximation.

Density Functional Theory & Multiple Scattering Theory

Density functional theory (DFT)

$$\left[-\frac{1}{2}\frac{\hbar}{m_e}\nabla^2+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{2}\int\frac{\rho(r')}{|r-r'|}dr+\sum_I^{N_I}\frac{Z_I}{|r-R_I|}\right)+\frac{\delta E_{XC}[\rho(r)]}{\delta\rho(r)}\right]\varphi_i(r)=\epsilon_i\varphi_i(r).$$

$$\rho(r) \quad = \quad \sum_i |\varphi_i(r)|^2$$

- Formulated in terms of stationary electronic wave functions and charge densities.
- Applicable to ordered structures only.

Multiple scattering theory (MST)

$$\det|t^{-1}(E)-G^0(q,E)|=0,$$

$$\rho(r)=-\pi^{-1}\ \mathrm{Im}\oint G_{II}(r,E)dE$$

- Formulated in terms of Green's functions G and scattering matrices t.
- Can be combined with CPA to address chemical disorder in small unit cell.

- Both methods are applicable to ordered structures.
- Disorder can be addressed using large supercells.
- Computational cost increases with number of electrons.

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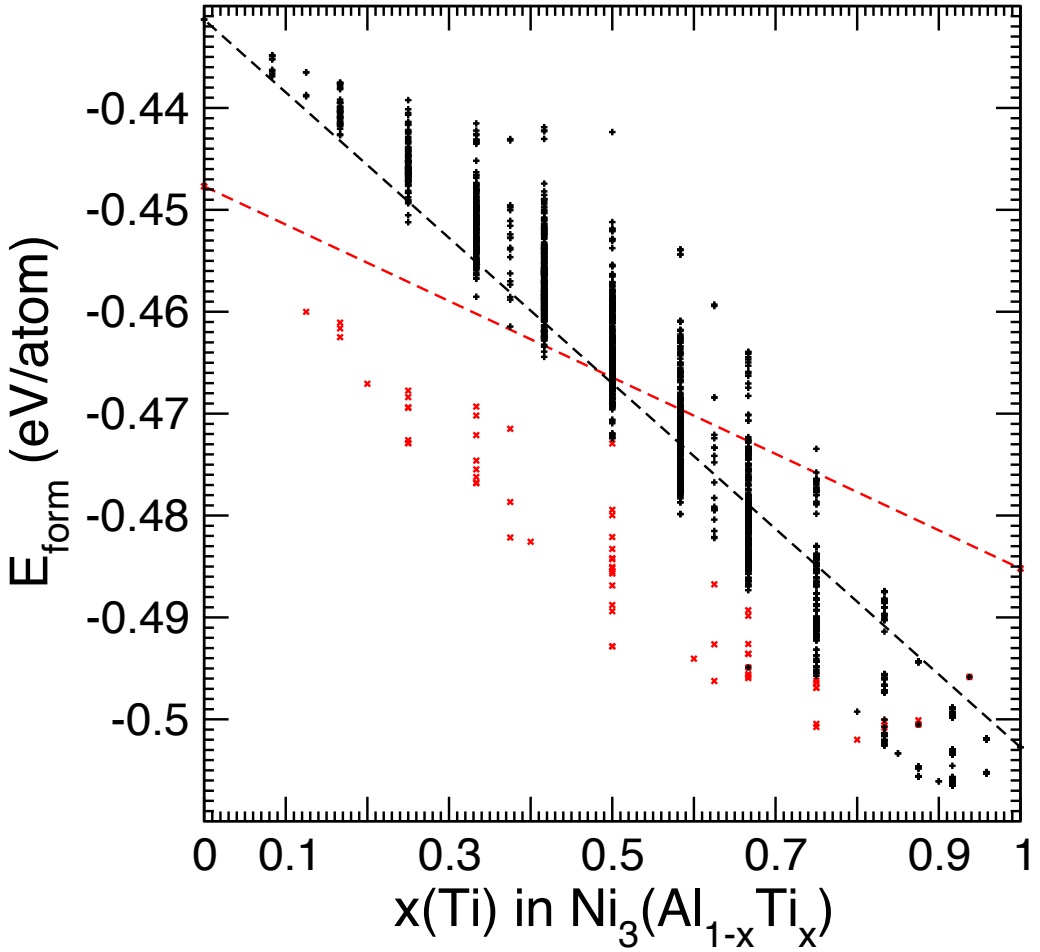
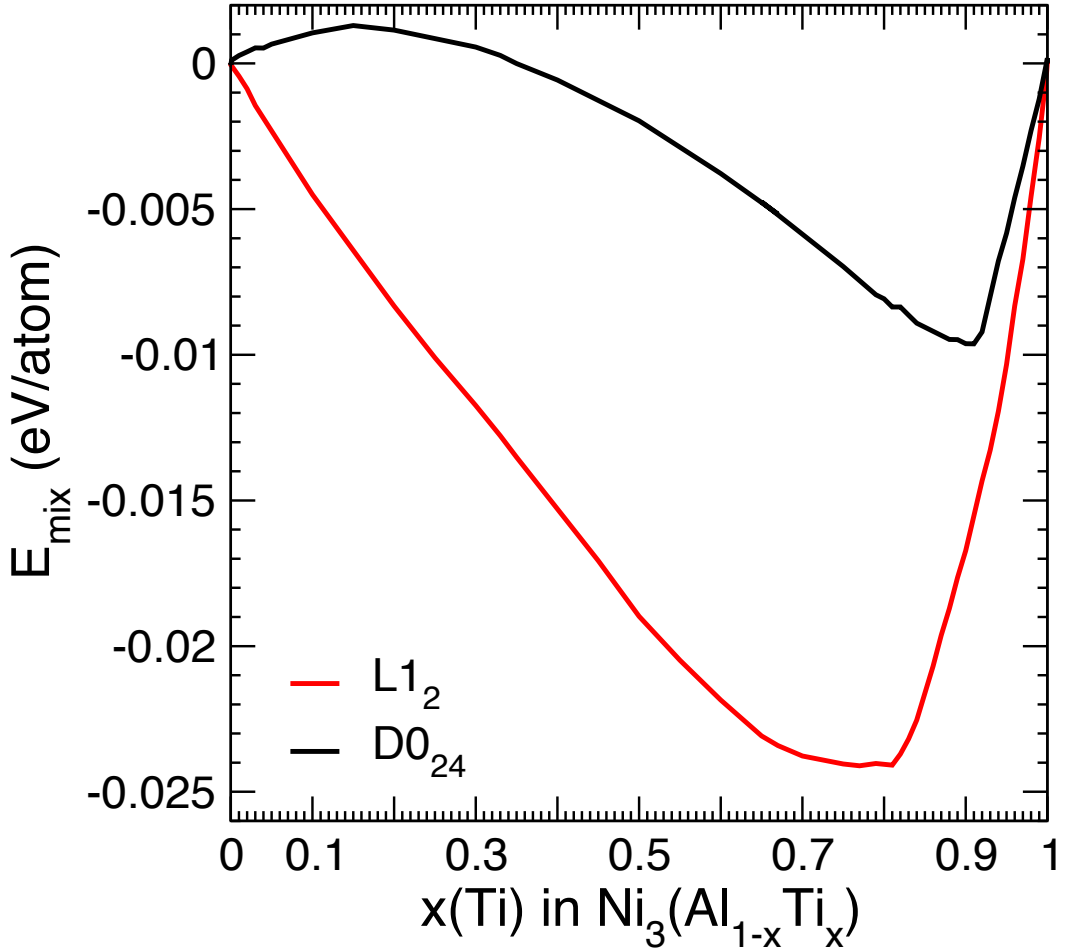
Combining formation and mixing energies

Formation energy from DFT



E_{form} is relative to energies of elemental solids.

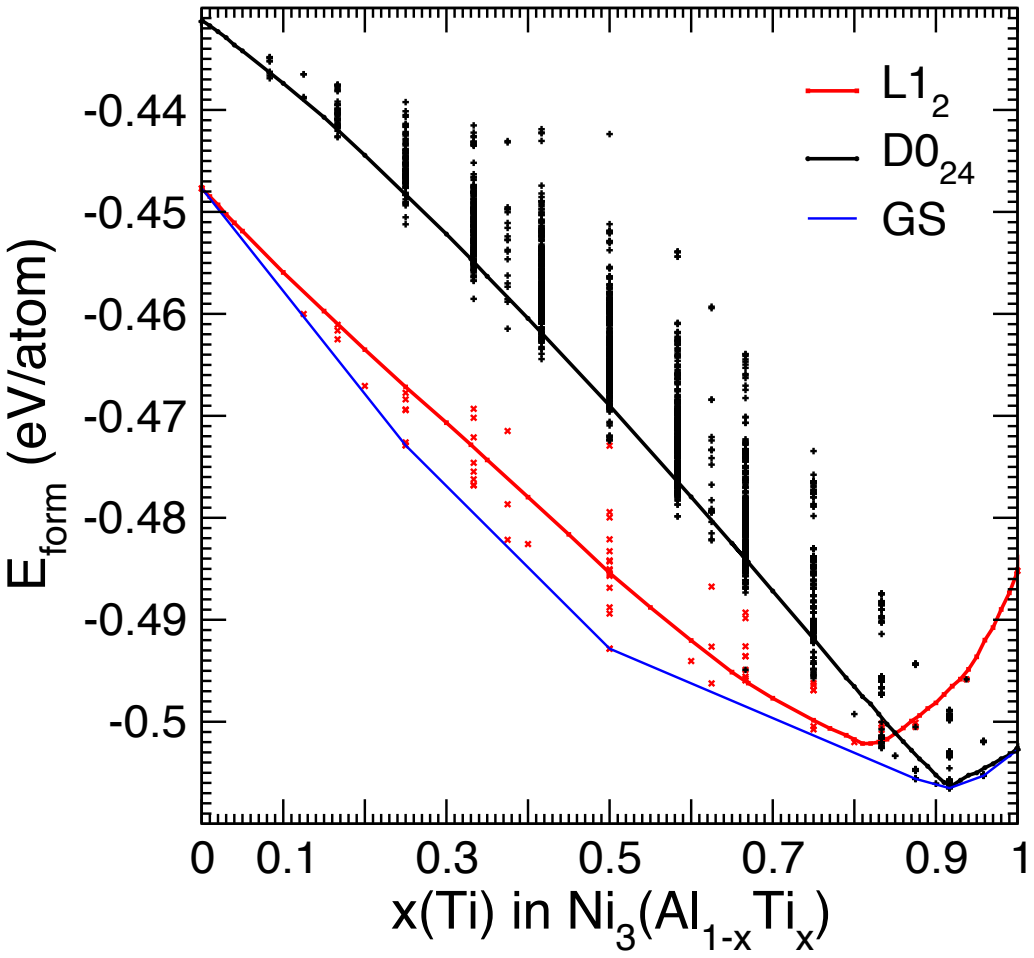
Mixing energy from MST+CPA



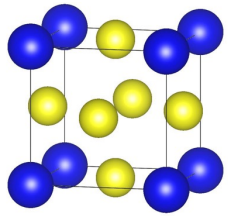
E_{mix} is relative to energies of terminal compositions.

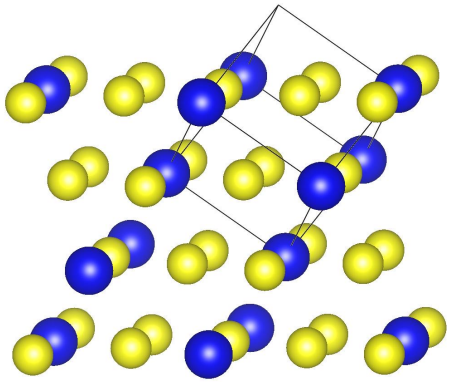
Formation energies in $Ni_3(Al,Ti)_1$ alloys

DFT + MST on the same energy scale.

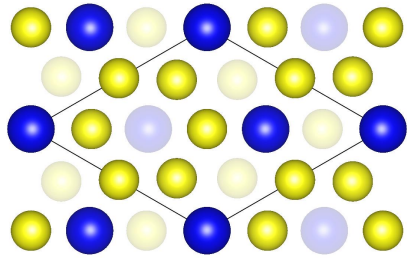


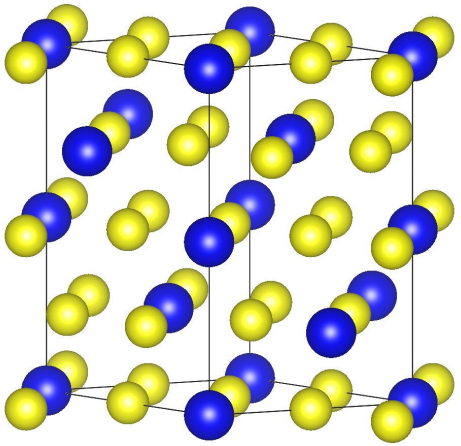
$L1_2$





$D0_{24}$





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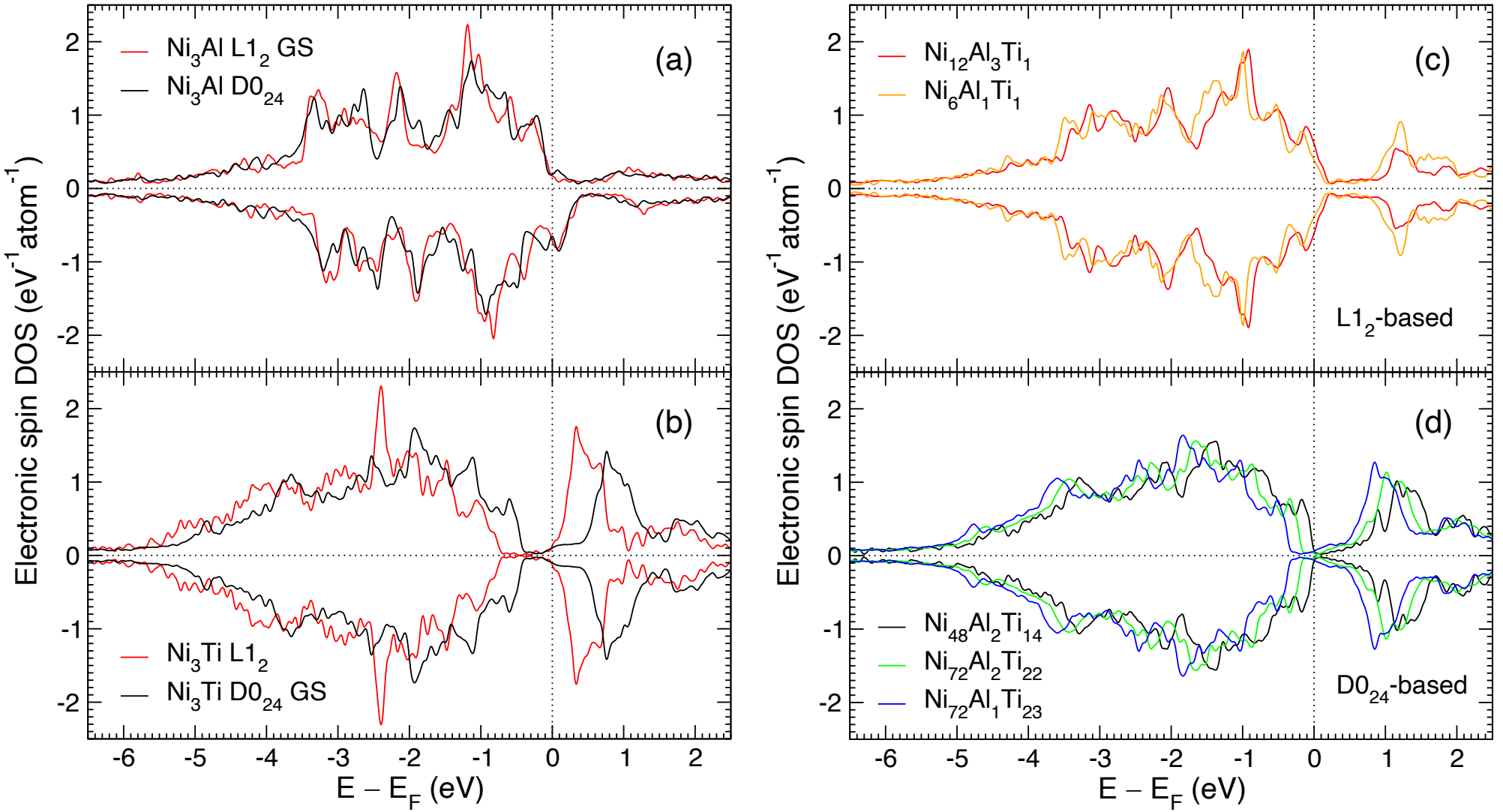
Electronic density of states (DOS) in $Ni_3(Al_{1-x}Ti_x)$



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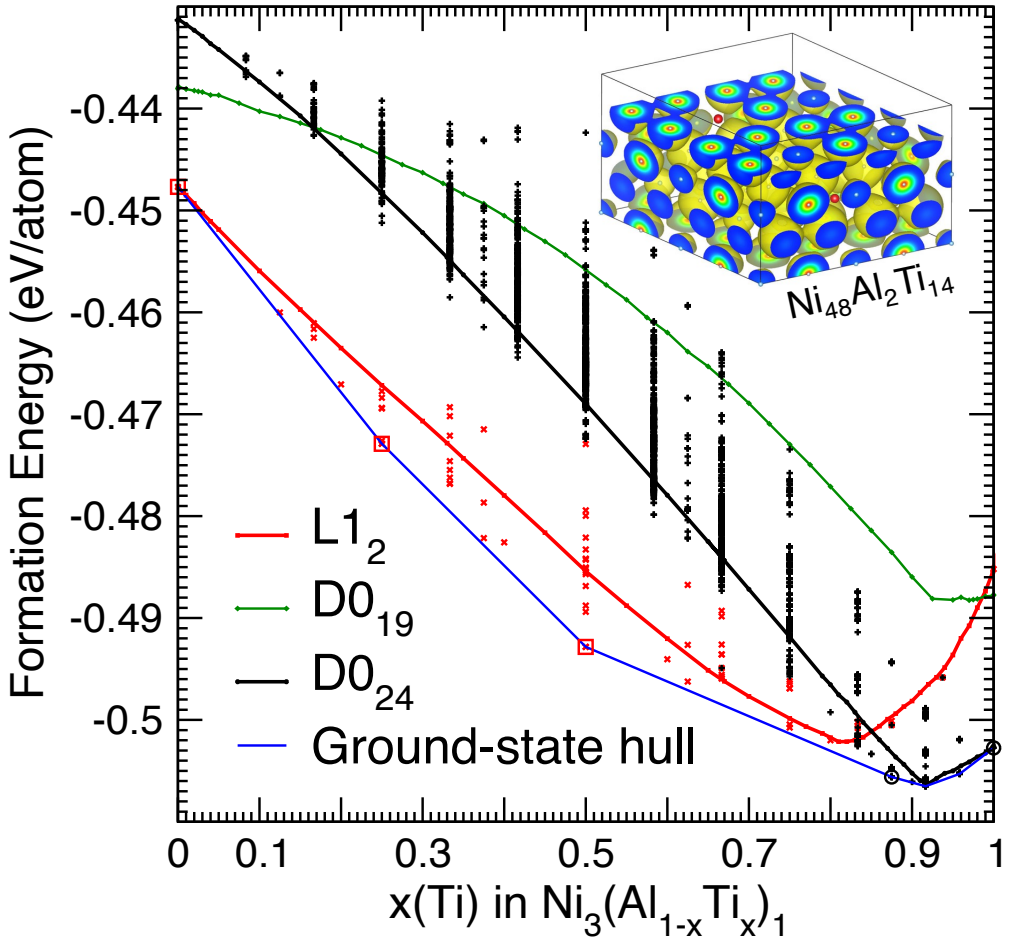
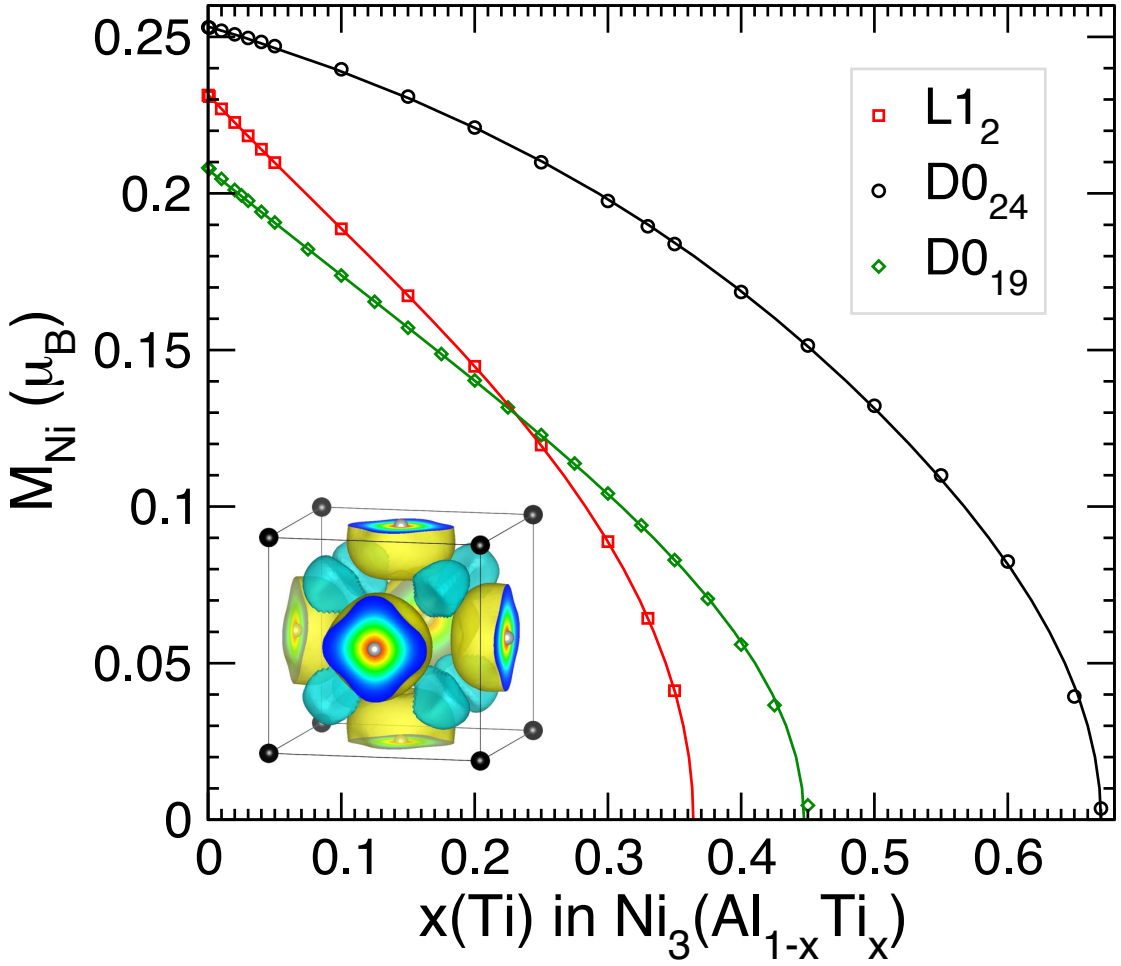
Phase transitions in $Ni_3(Al,Ti)_1$ alloys

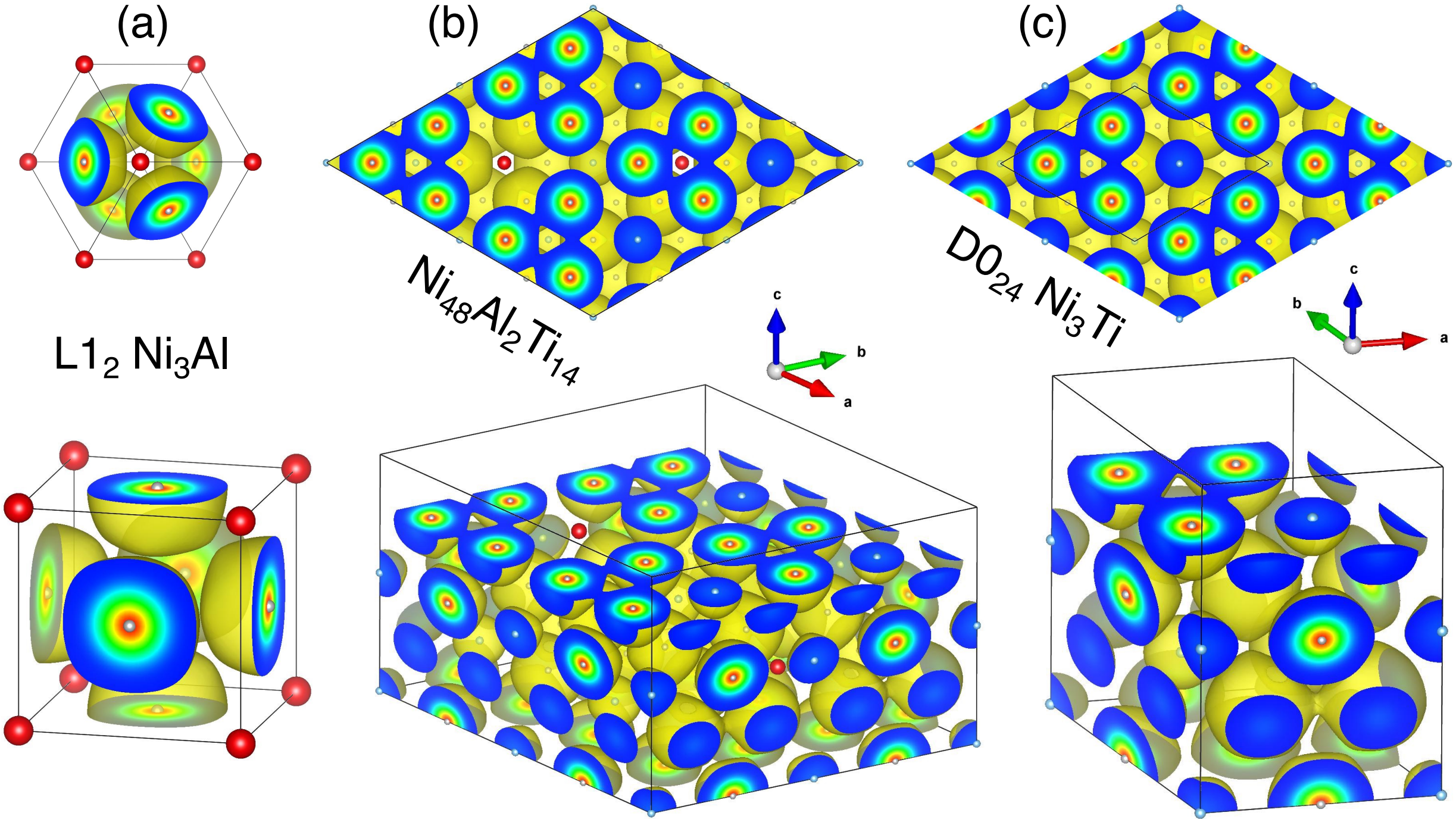
Structural stability



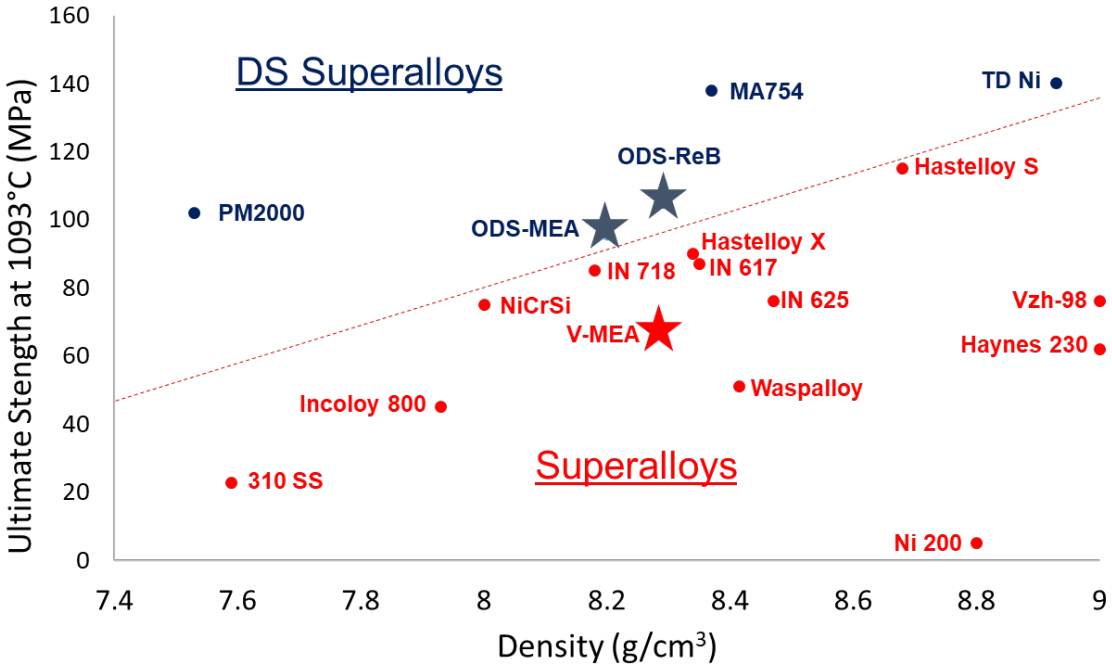
Magnetism



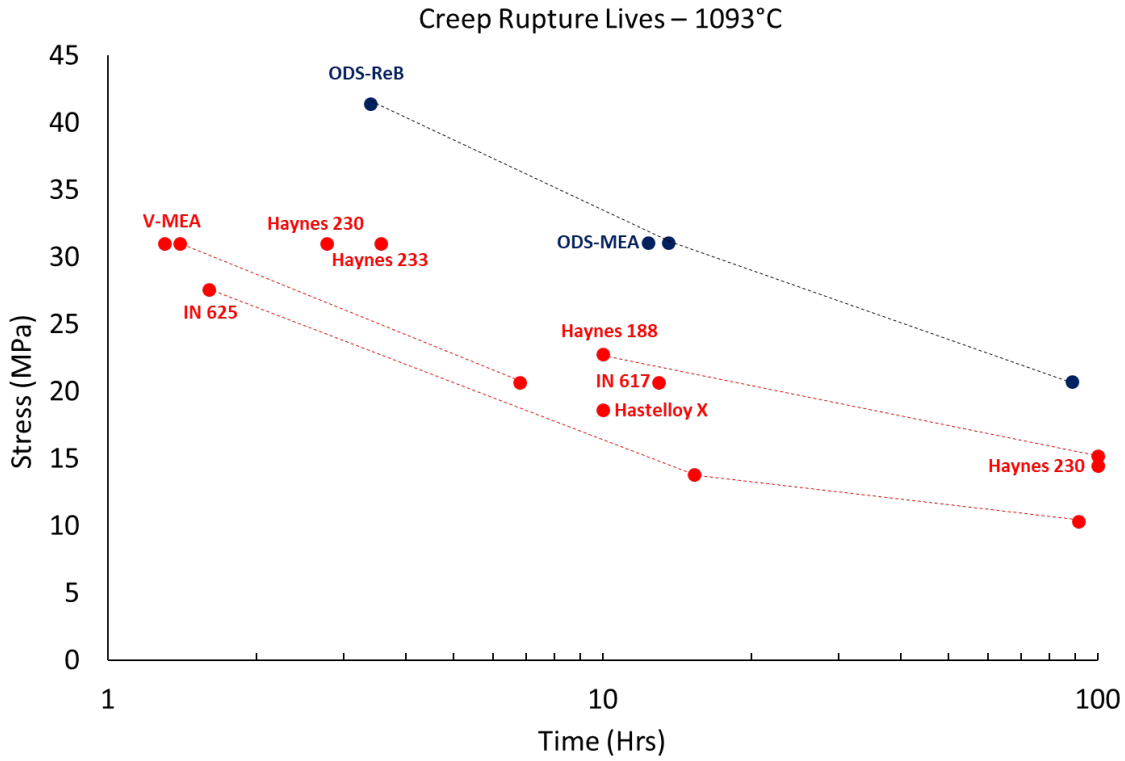
Structural, electronic, and magnetic transitions.


(a)
(b)
(c)
$L1_2$ Ni_3Al
$Ni_{48}Al_2Ti_{14}$
DO_{24} Ni_3Ti
c
b
a
c
b
a

Experimental strength of alloys



Scatter plot of alloy density and ultimate tensile strength at 1093°C for conventional and dispersion strengthened alloys. V-MEA, ODS-MEA and ODS-ReB are denoted by star points.

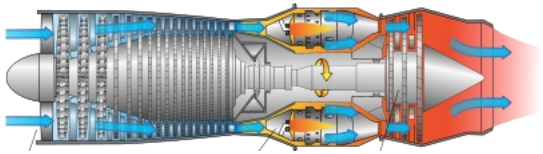


Scatter plot of creep rupture life (hours) and stress (MPa) at 1093°C for conventional superalloys.
ODS-MEA and ODS-ReB are denoted by blue points.

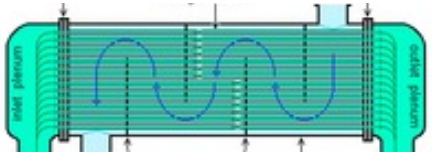
✓ Best-in-class alloys are designed.

Applications of superalloys

Combustion engines



Heat exchangers



Turbines

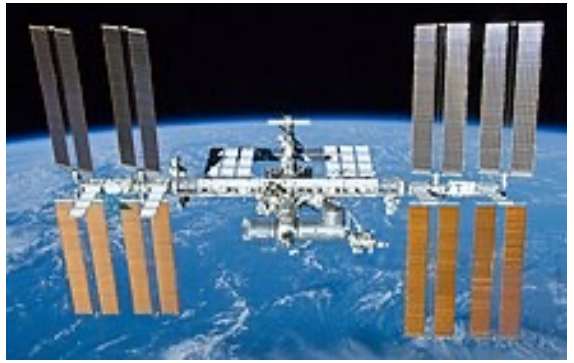
Generators

Nuclear reactors

Power plants

Planes, trains, automobiles

Satellites



Ships, Submarines

Rockets

Superalloys retain strength at high temperature, stress, radiation.
Electric and thermal conductivity of a metal, corrosion resistance.
Superalloys are used in engines, nuclear reactors, heat exchanges.

Summary

- Considered subtraction of systematic errors.
- Combined full-potential DFT and multiple-scattering theory with CPA;
- Applied to precipitation in Ni superalloys.
- Formation of χ and η phases along the γ′ stacking faults correlates with improved creep strength of Ni superalloys.
- Composition-structure-property relations allow to design an alloy with superior strength and creep properties at high operating temperature.
- Subtraction of systematic errors resulted in higher-accuracy predictions, useful for materials design.

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Publications

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