

Study on Energy of Formation of NiTi and NiZr Intermetallic compounds using DFT

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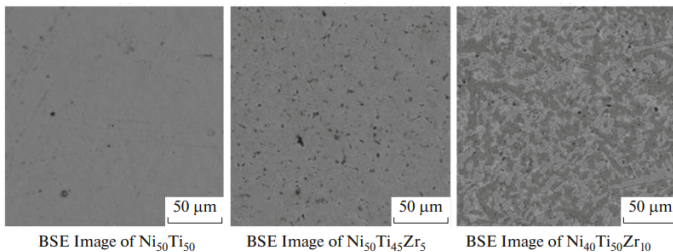
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Objective

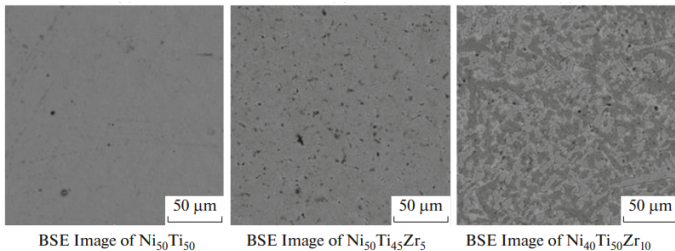
- To study the crystallographic information of NiTi and NiZr system.
- To optimize the cut-off energy and k-points for NiTi and NiZr system using single point energy calculation.
- To determine the ground state energy of Ni-FCC, Ti and Zr in HCP, NiTi-B2 and NiZr-orthorhombic crystal structure using geometric optimization.
- To determine the energy of formation of NiTi and NiZr and compare with literature data.

Why add Zr to Nitinol?



Back Scattering Electron Images [2]

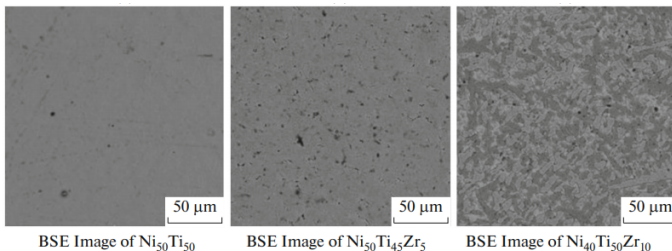
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Property	Ni(50)Ti(50)	Ni(50)Ti(45)Zr(5)	Ni(40)Ti(50)Zr(10)
Hardness (VPN)	194	359	535

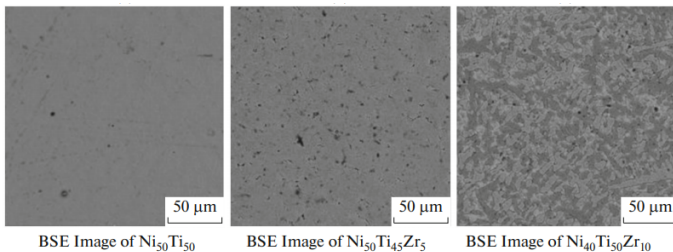
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% Shape memory effect	75%	31%	25%

Density Functional Theory

Time Independent Schrodinger Equation: $\hat{H}\psi(R_I, r_i) = E\psi(R_I, r_i)$

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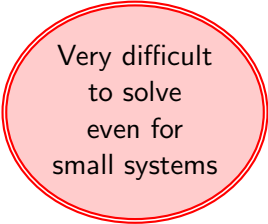
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Approximations!

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Electronic Hamiltonian: $\hat{H} = \hat{T}_e + \hat{V}_{e-N} + \hat{V}_{e-e}$

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Energy represented as a functional of electron density.

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Treats density as the basic variable: the external potential determines uniquely the charge density, and the charge density determines uniquely the external potential $E[\rho(\mathbf{r})]$.

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Treats density as the basic variable: the external potential determines uniquely the charge density, and the charge density determines uniquely the external potential $E[\rho(\mathbf{r})]$.

A universal functional for the energy $E[\rho(\mathbf{r})]$ can be defined in terms of the density. The exact ground state is the global minimum value of this functional.

$$E[\rho(\mathbf{r})] \geq E[\rho_0(\mathbf{r})]$$

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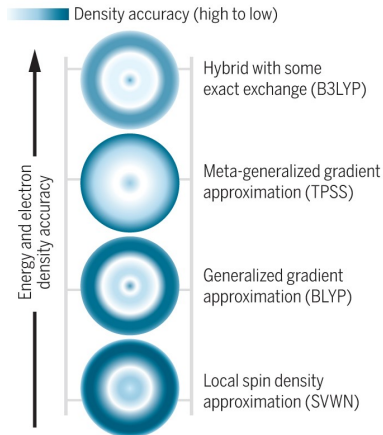
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Density Functional Theory

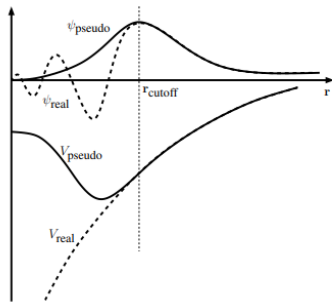
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Pseudopotential Approach

Softwares involved

- Quantum ESPRESSO: Open-Source software for electronic-structure calculations and materials modeling based on density-functional theory, plane waves, and pseudopotentials.

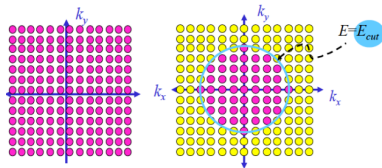


- BURAI: A GUI for Quantum ESPRESSO

Experimental Calculations

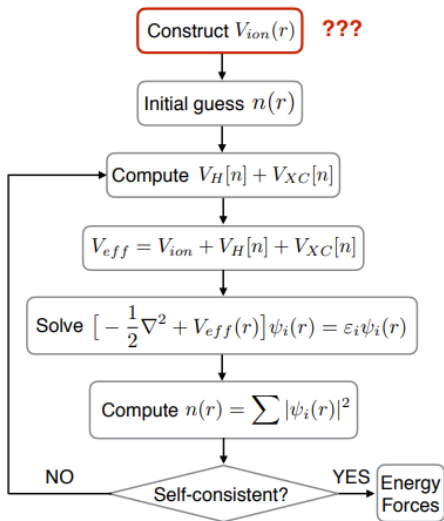
- Download the particular CIF.
- Perform fixed cell calculation for optimization of E_{cut} and k-points.

$$\frac{1}{2}|\mathbf{k} + \mathbf{G}|^2 \leq E_{cut}$$



- Perform vc-relax calculation for optimization of the geometric cell.
- Calculate the energy of formation for NiTi and NiZr.

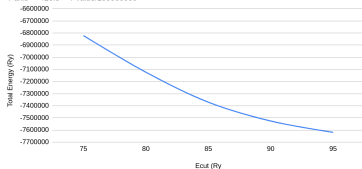
Experimental Calculations



Total Energy Calculation Results

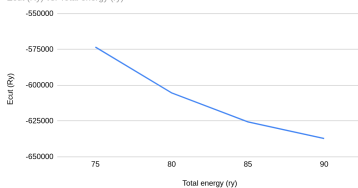
Ni Ecvt convergence

Y-axis = $-426.5 + Y\text{-value}/100000000$

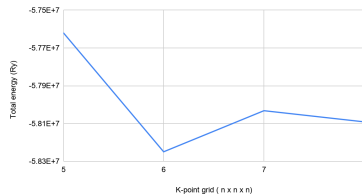


NiTi Ecvt convergence

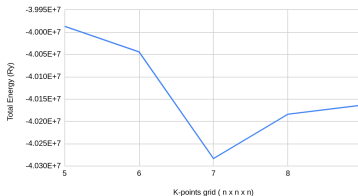
Ecvt (Ry) vs. Total energy (ry)



Ni K-point convergence



NiTi k-point convergence



Total Energy Calculation Results

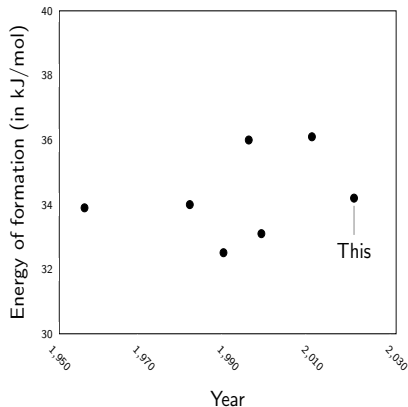
- Ni (FCC) = -426.5321 Ry
- Ti (HCP) = -181.7691 Ry
- Zr (HCP) = -303.0994 Ry
- NiTi (B2) = -608.4033 Ry
- NiZr (Orthorhombic) = -729.75205 Ry

Energy of Formation Calculation Results

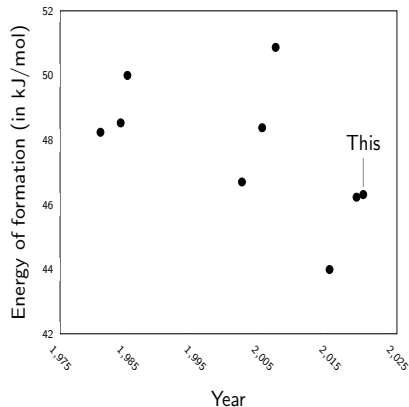
$$\Delta E_{A_p B_q} = \frac{1}{p+q} E_{A_p B_q} - \frac{p}{p+q} E_A - \frac{q}{p+q} E_B$$

- $\Delta E_{NiTi} = -34.1971 \text{ kJ/mol}$
- $\Delta E_{NiZr} = -46.3072 \text{ kJ/mol}$

Comparison with Previous Literature Data



Data for NiTi



Data for NiZr

Conclusions

- The binary compound NiTi is in B2 crystal structure with 2 atoms in the primitive cell and NiZr in orthorhombic crystal structure with 4 atoms in the primitive cell.

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- The binary compound NiTi is in B2 crystal structure with 2 atoms in the primitive cell and NiZr in orthorhombic crystal structure with 4 atoms in the primitive cell.
- The required cut-off energy and k-point for geometric optimisation are calculated by series of single point energy calculation.
- The calculated energy of formation of standard reference state structure of NiTi and NiZr at 0K are comparable with literature data.

References



HAMMES-SCHIFFER, S.

A conundrum for density functional theory.

Science 355, 6320 (2017), 28–29.



KHAN, A. N., MUHYUDDIN, M., AND WADOOD, A.

Development and characterization of nickel–titanium–zirconium shape memory alloy for engineering applications.

Russian Journal of Non-Ferrous Metals 58, 5 (2017), 509–515.

Thank you for your time.
Questions?