materials design

NRC ALLOY 690 RESEARCH MEETING

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Thermal Embrittlement of Nickel and Iron-Base Alloys: Mechanistic Understanding and Life Prediction from Ab Initio Computations

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Materials Design, Inc.

Outline

- Ab initio calculations as part of integrated computational materials engineering
- Examples and Validation:
  - Long-range ordering in Ni-Cr alloys
  - $\alpha+\alpha'$ decomposition in Fe-Cr alloys
  - Diffusion
  - Solubility products
- Perspectives
- Discussion

Role of Simulations

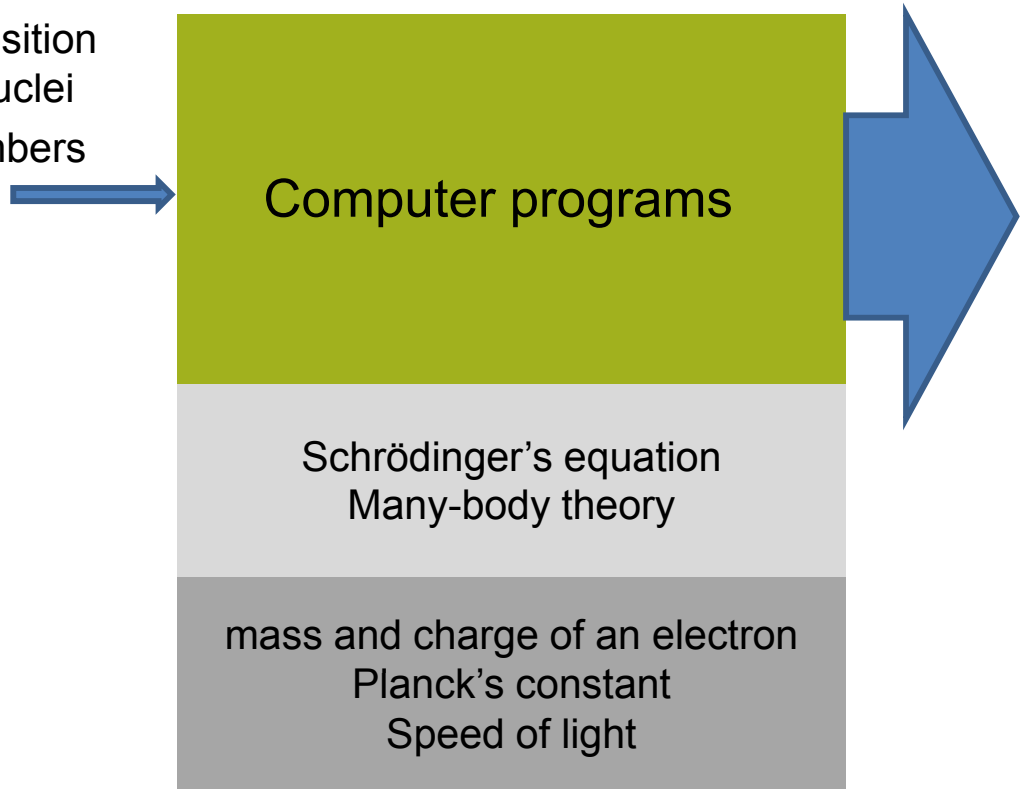
MODELING AND SIMULATIONS ARE NEEDED:

- Experiments are too long, too costly, and they do not provide direct insight into mechanisms
- Inability to accelerate embrittlement kinetics by increasing temperature
- Ability of simulations to study individual effects (e.g. one alloying element at a time)
- Computations are getting more accurate and cost effective all the time

Ab Initio Calculations

Input:

- Arbitrary position of atomic nuclei
- Atomic numbers

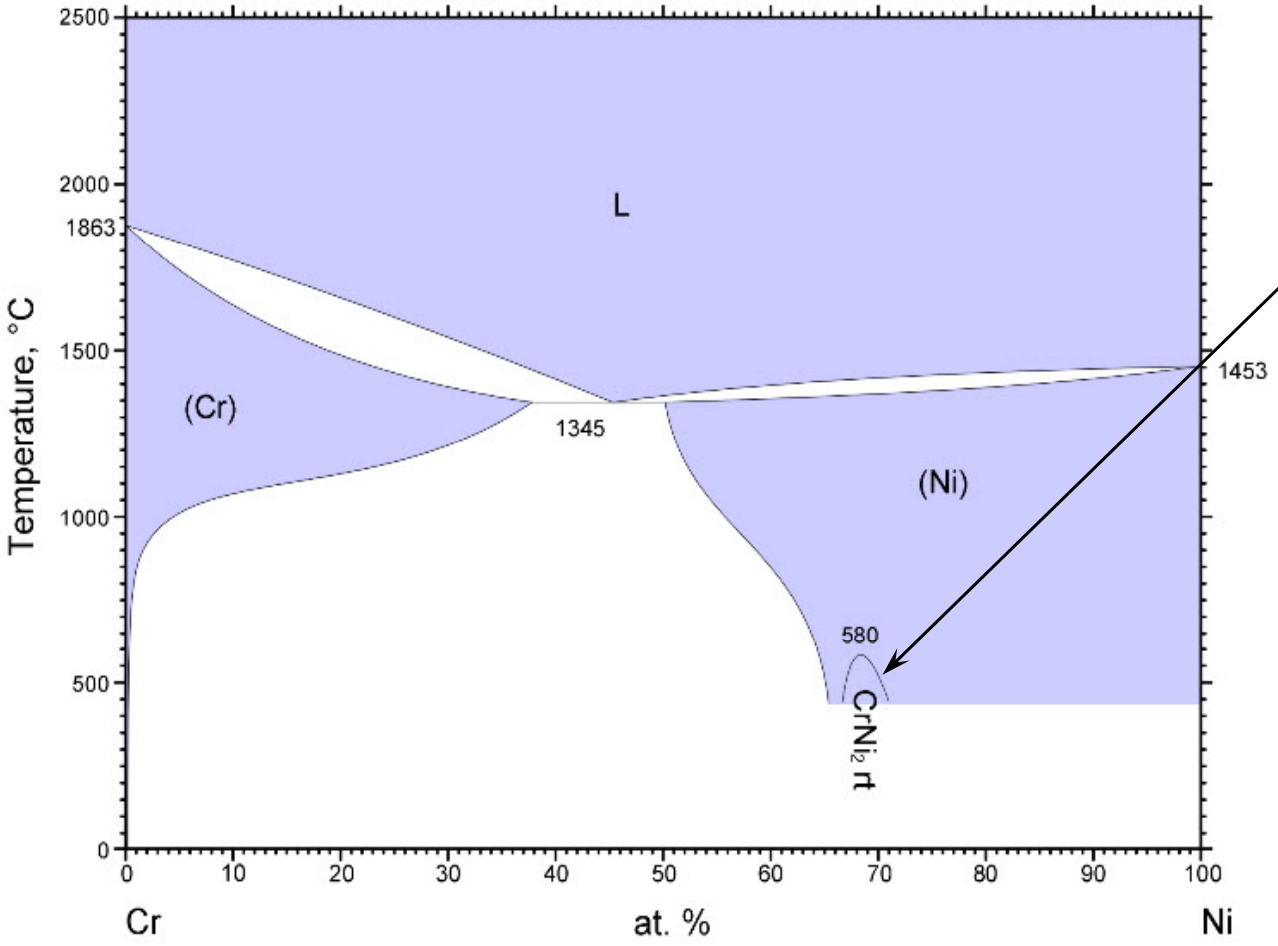


Output:

- Structure and thermodynamic stability of phases
- Surface energies
- Grain boundary energies
- Adsorption energies
- Reaction barriers
- Diffusion rates
- Defect energies
- Electronic, optic, and magnetic properties
- …

Examples and Validation

Long Range Order in Ni-Cr Alloys



Ni_2Cr phase embrittles

Empirical evidence [1] indicates that Fe impedes formation of LRO Ni_2Cr phase

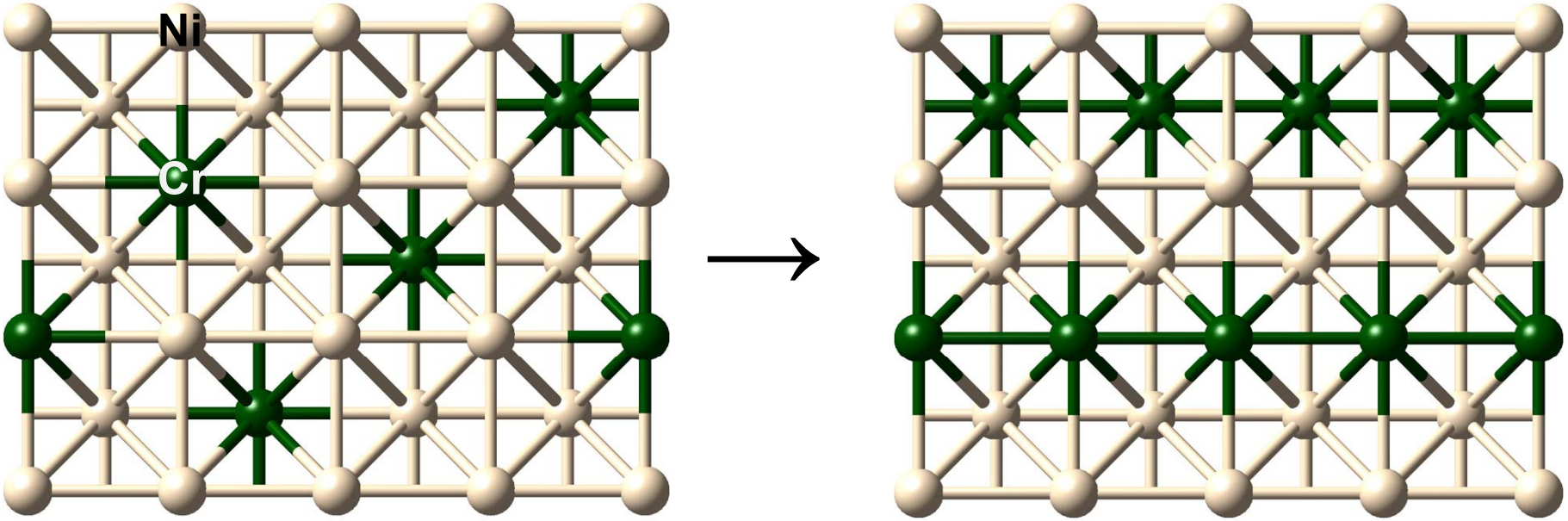
What is the effect of other alloying elements such as Nb, Mn, and Mo?

1. Delabrouille et al., 14th Intl. Conf. on Environmental Degradation of Materials in Nuclear Power Systems, Virginia Beach, VA, August 23-27 (2009)

Ni-Cr Alloy

disordered

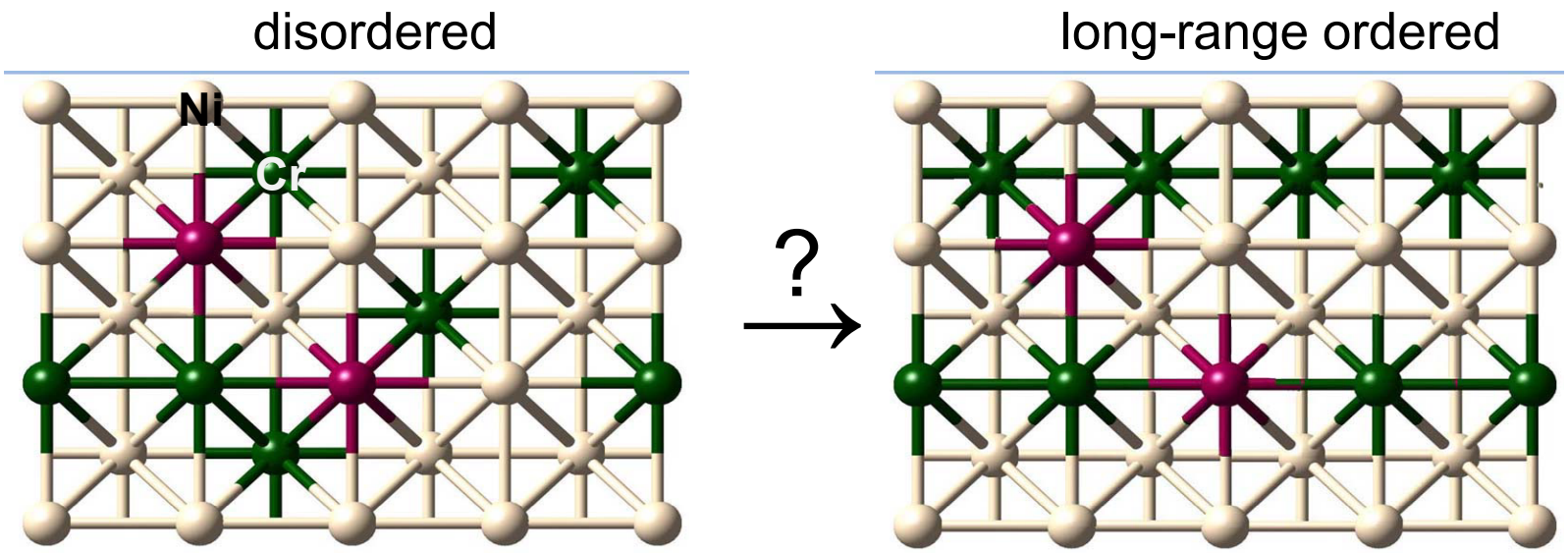
long-range ordered



Random Ni-Cr alloy stable at elevated temperatures

Long-range order stabilized at lower temperatures by energetically preferred Cr-Cr pairing

Effect of Alloying Element



Fe	59 kJ/mol	effective
Mn	37	effective
Nb	29	effective
Mo	3	indifferent

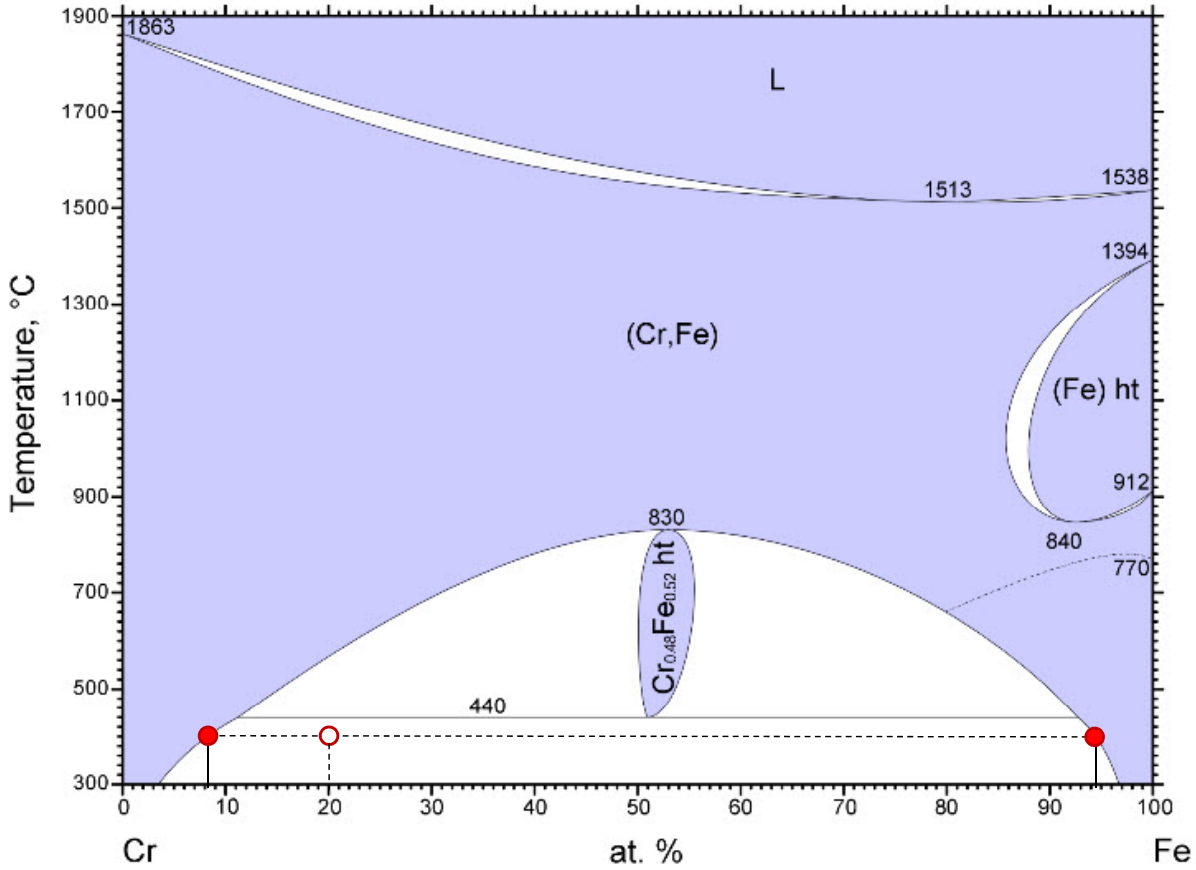
Computations are consistent with and explain experimental data [1]

1. G. A. Young et al. 14th Intl. Conf. on Environmental Degradation of Materials in Nuclear Power Systems, Virginia Beach, VA, August 23-27 (2009)

Long Range Ordering

- Computations indicate that the effect of Fe, Mn, and Nb alloying elements impeding long range order are due to **thermodynamic** destabilization of ordered phase; Mo has little influence on the thermodynamic stability of the ordered phase
- The ordering process is likely to involve vacancy or defect-assisted diffusion
- Ab initio calculations provide quantitative data on
  - Vacancy formation energies
  - Diffusion barriers and diffusion rates

α-α' Decomposition in Fe-Cr

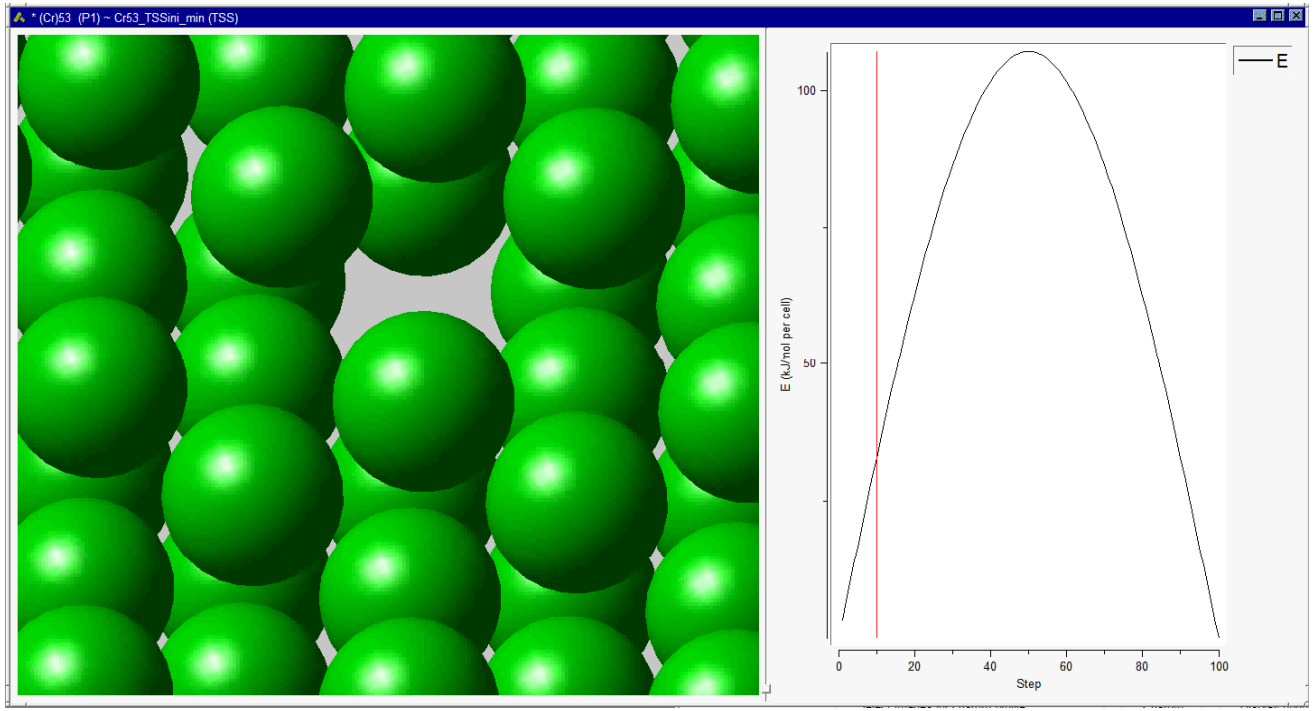


- Below 440 C an Fe-Cr alloy decomposes into a Cr-rich and an Fe-rich phase
- The rate of decomposition involves vacancy assisted diffusion

Vacancy Diffusion

Computed energy barrier for vacancy hopping

In Fe: 67 kJ/mol
In Cr: 108 kJ/mol



Diffusion

Computed energy barrier and jump rates for vacancies in Fe and Cr:

Barrier	Vacancy jumps per hour: at room temperature	at 500 K
in Fe: 67 kJ/mol	~10^{6}	~10^{11}
in Cr: 108 kJ/mol	~10^{-1}	~10^{6}

For the Ni-Cr system, Delabrouille et al. (2009) quote activation energies of 73 to 87 kJ/mol. They conclude: “For an alloy with 7.2% Fe, the time for initiation of LRO could be lower than the expected lifetime (60 years) depending on the activation energy”.

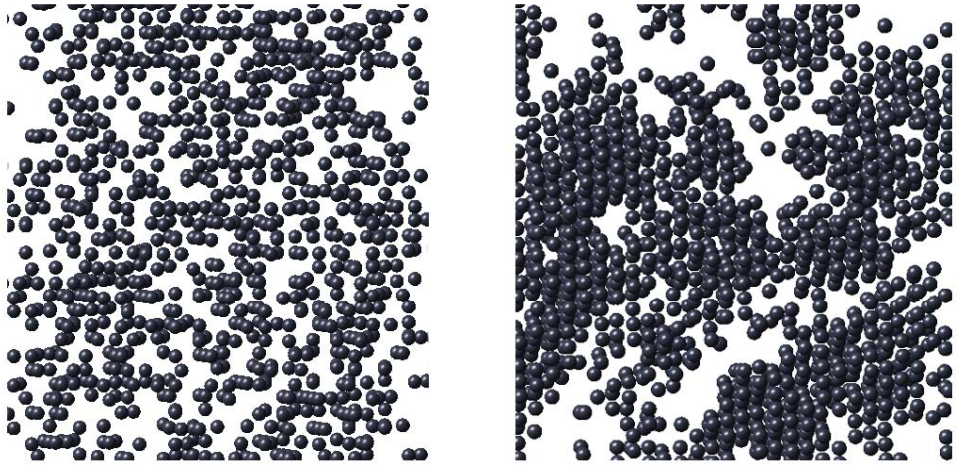
Note: It’s not just the activation energy, but the thermodynamic driving force and attempt frequencies that matter. Ab initio theory can provide these properties.

α-α' Decomposition in Fe-Cr

Fe-20Cr alloy

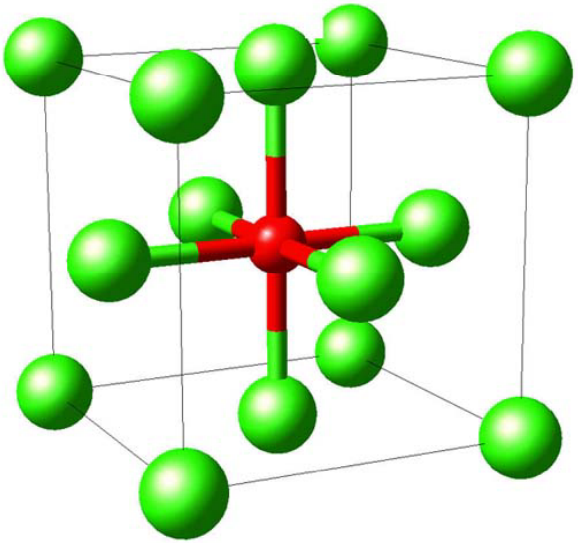
only Cr atoms are shown

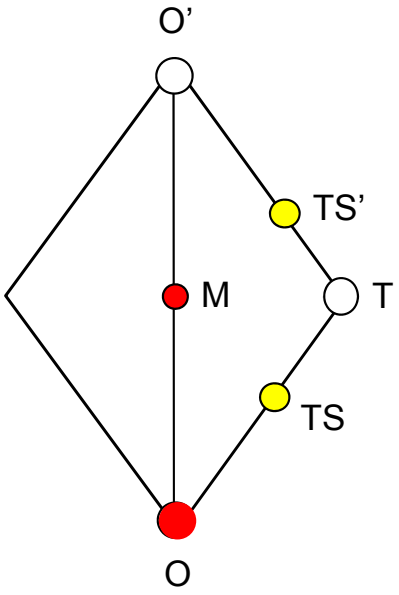
100 K

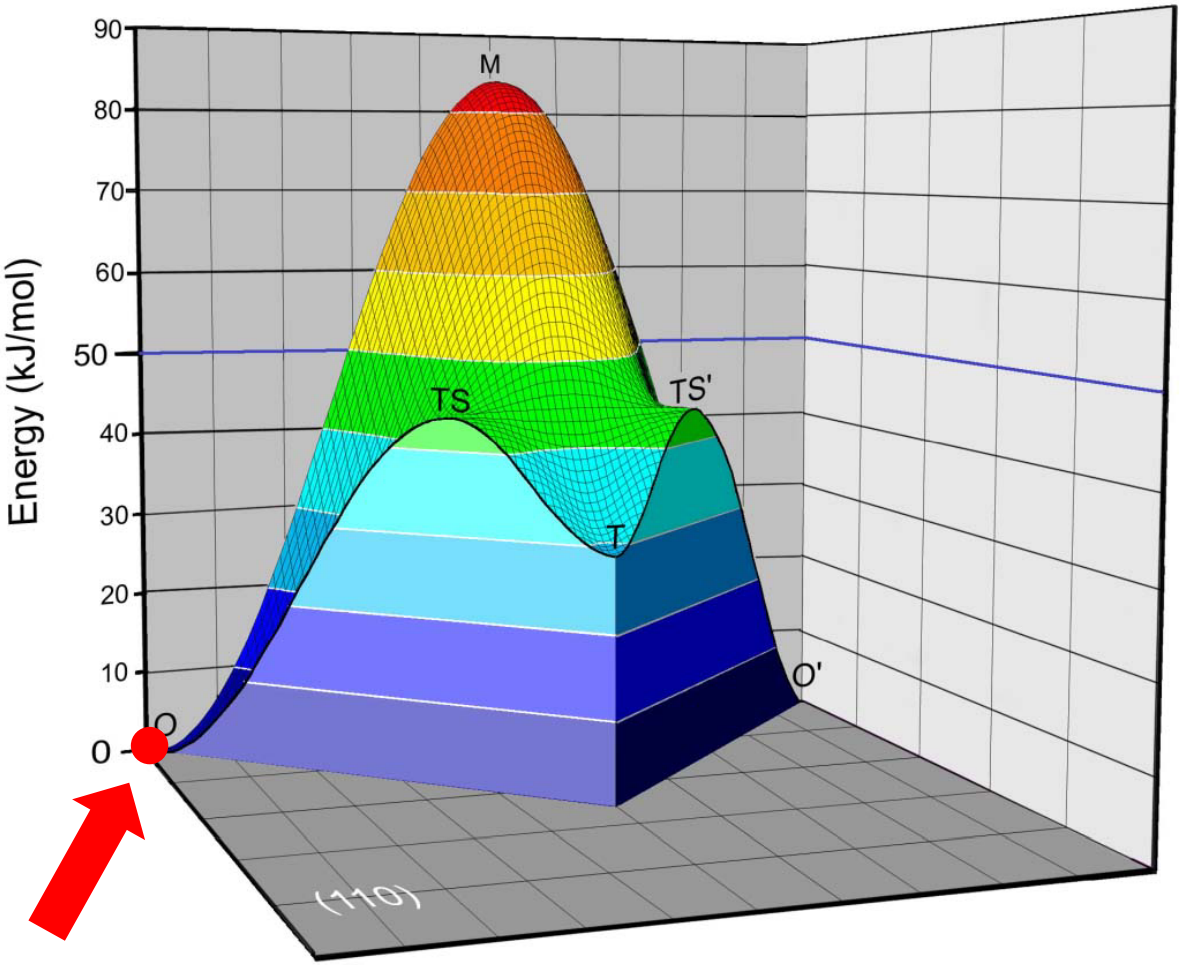


- Simulation of vacancy-mediated α-α' decomposition
- Kinetic Monte Carlo simulations based on ab initio data for environment-dependent energy and preferred local ordering and jump rates
- No separation at elevated temperatures
- Clear separation at low temperatures
- 600 million Monte Carlo moves

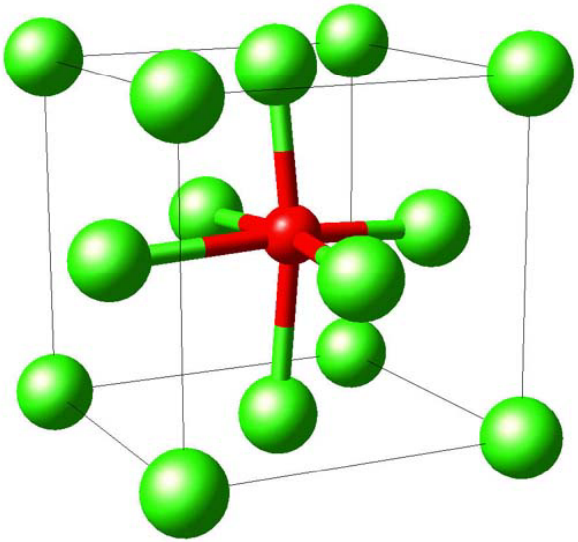
Validation: Diffusion of H in Ni

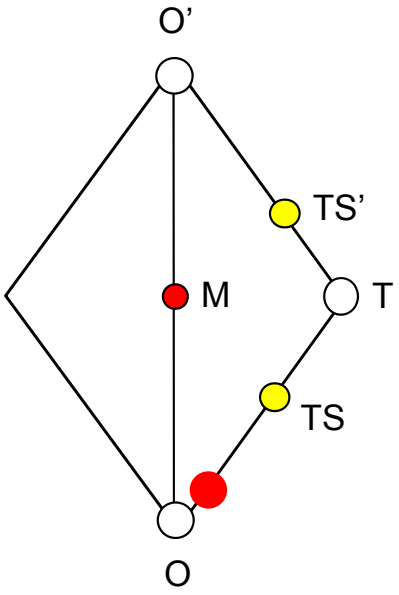


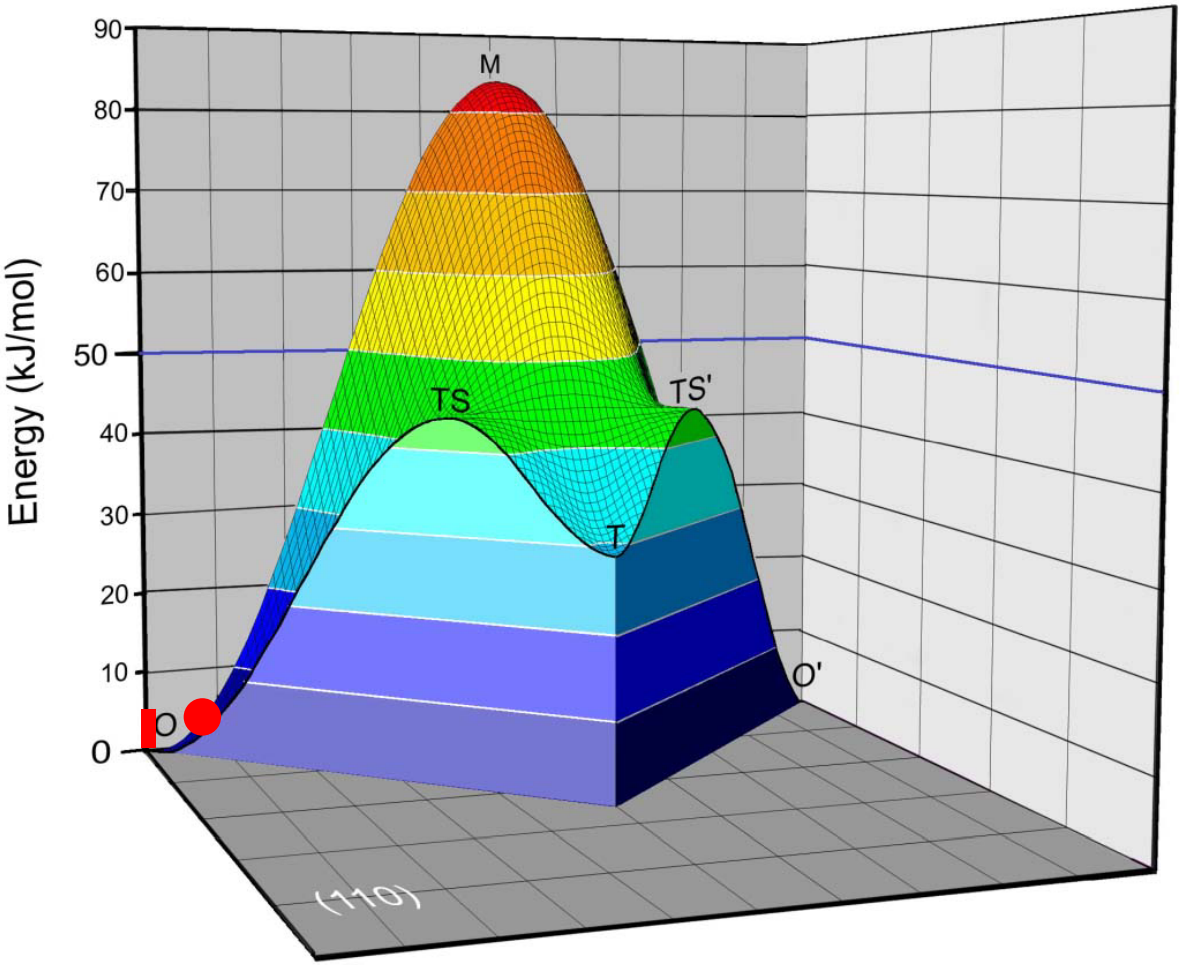




Diffusion of Interstitial Impurities







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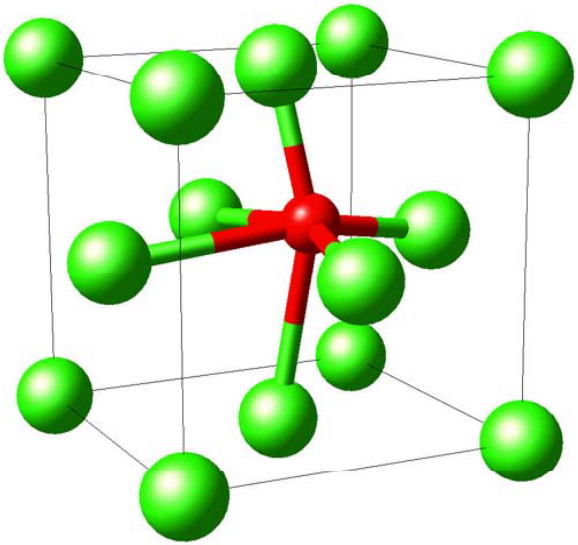

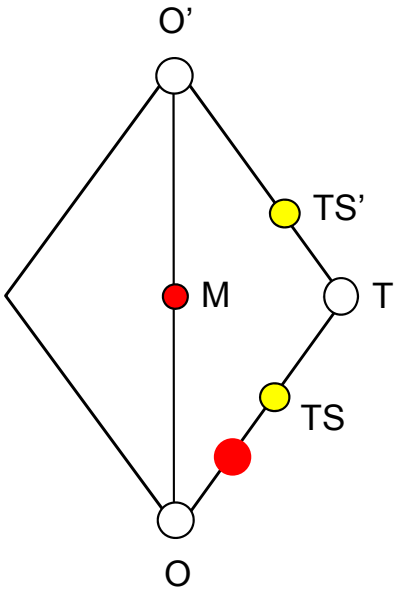

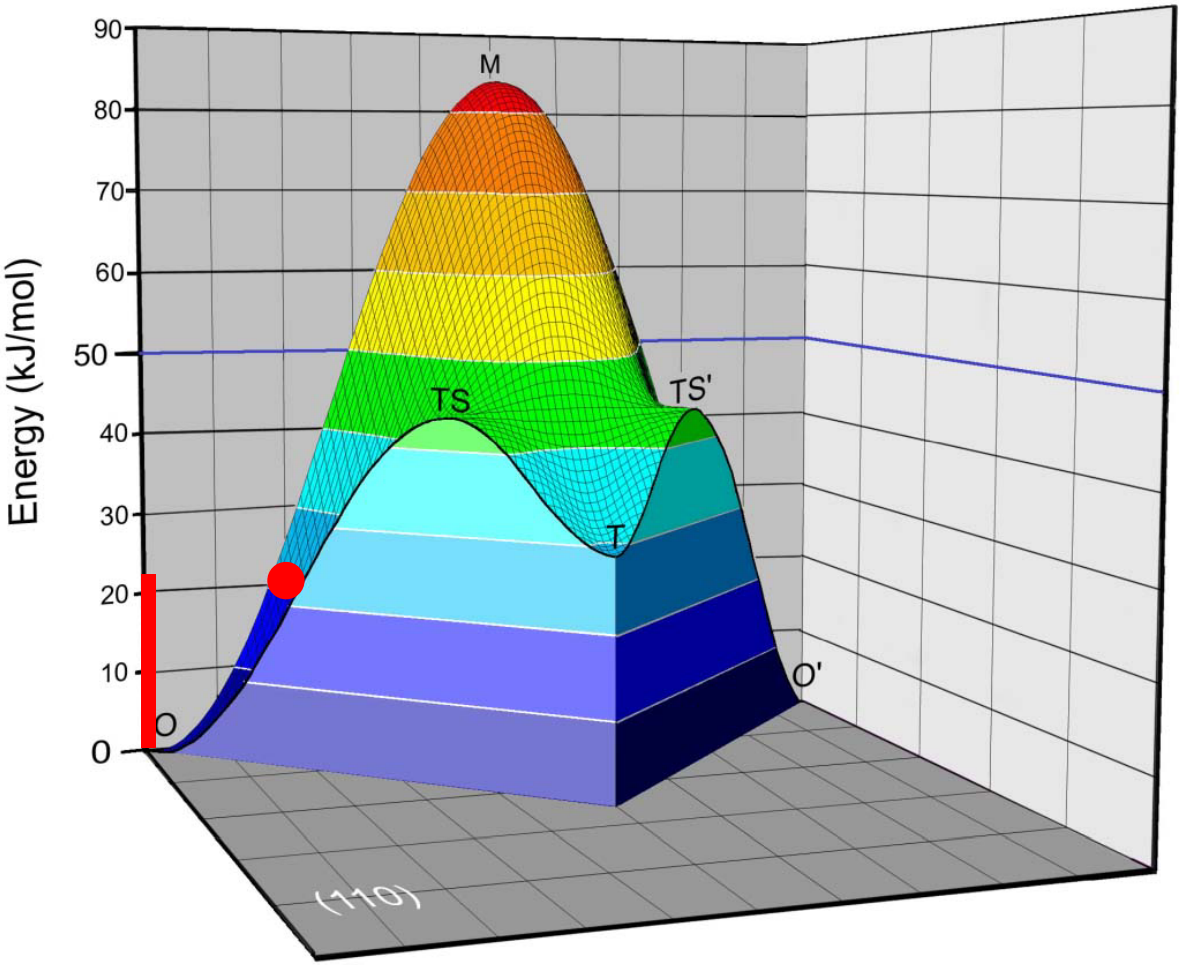

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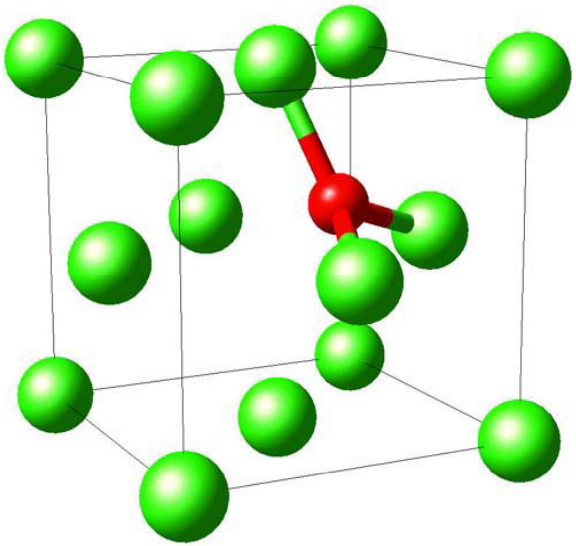

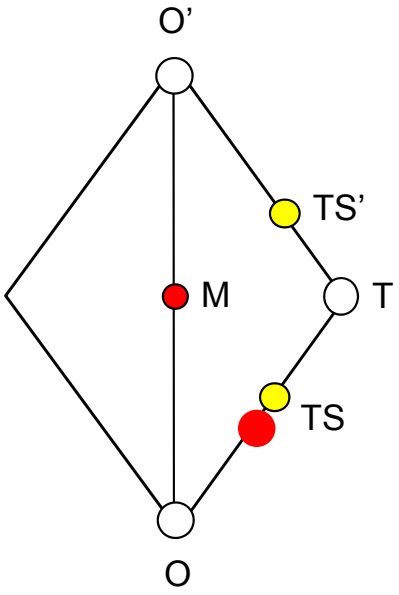

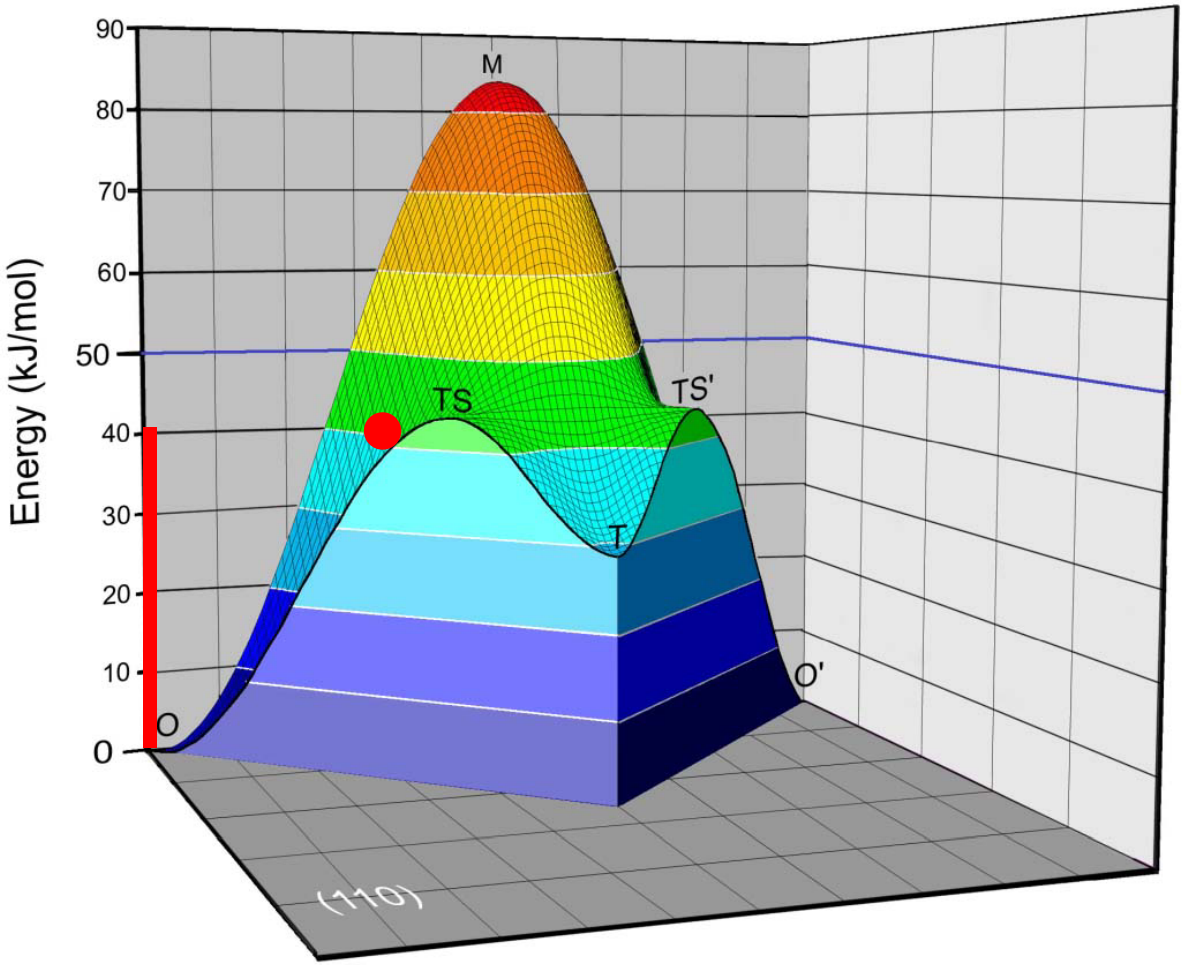

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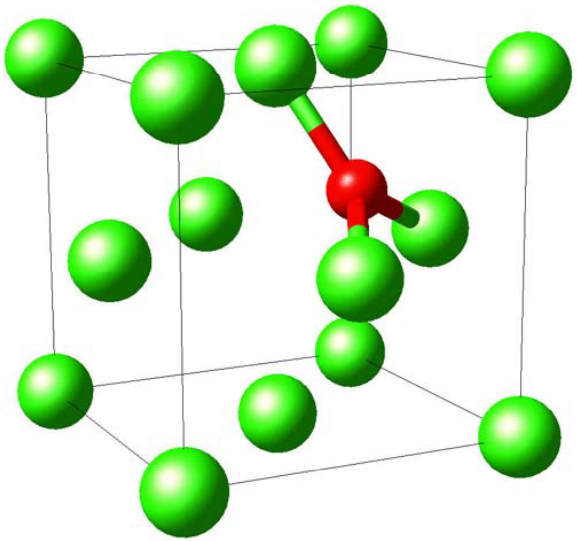

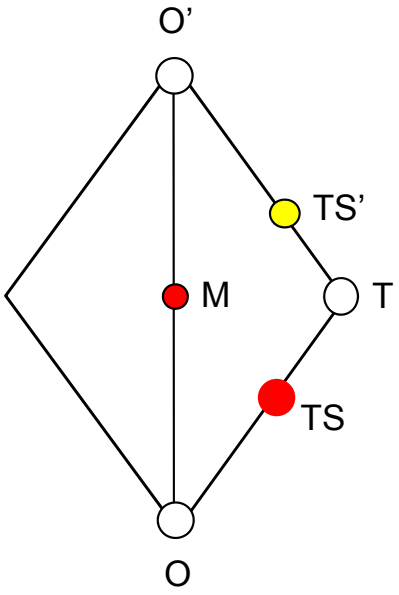

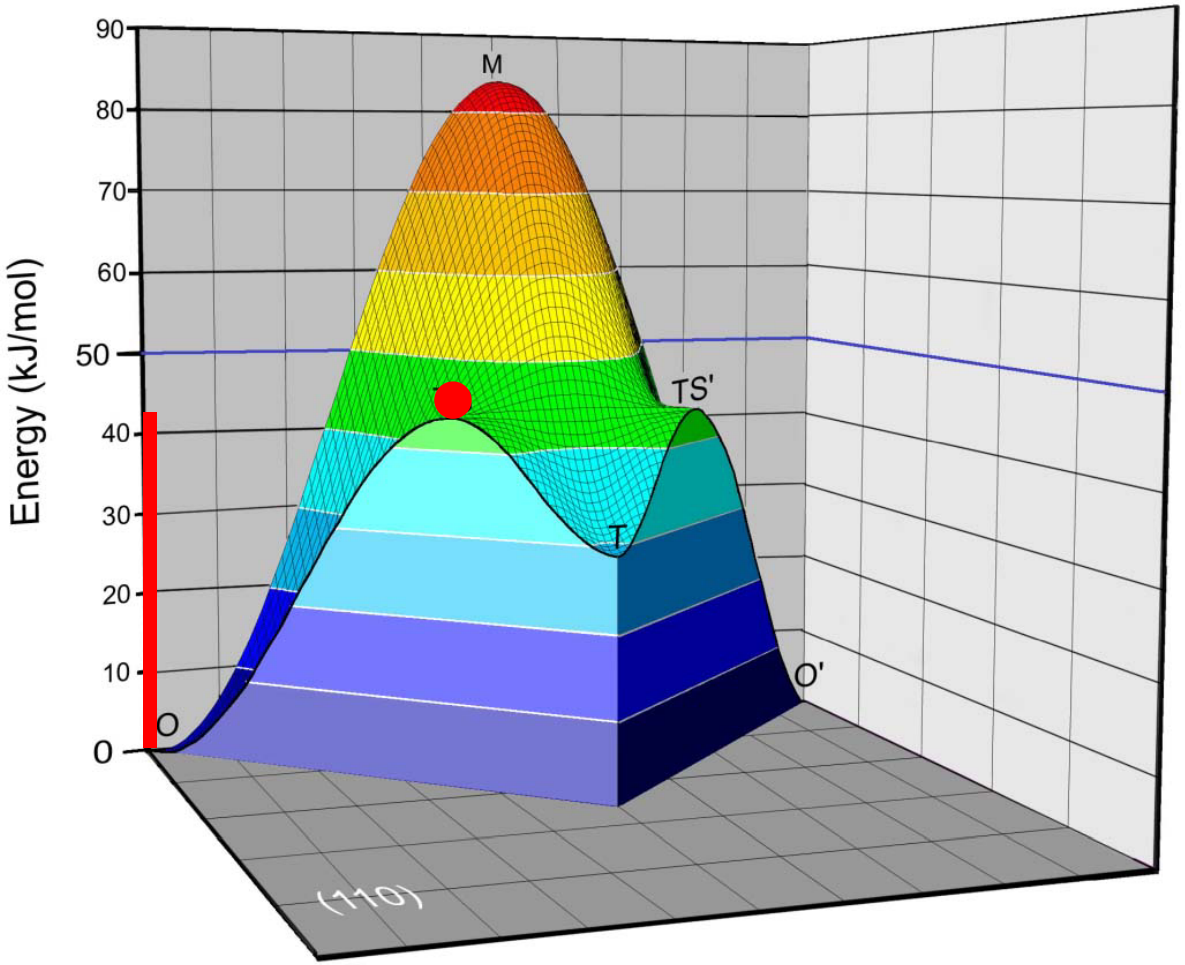

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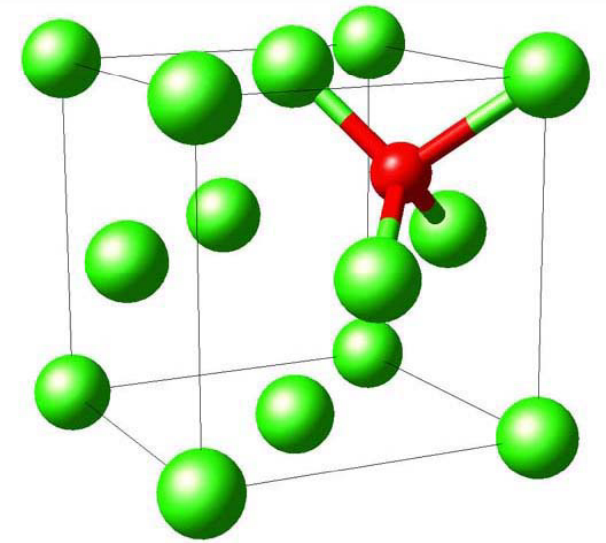

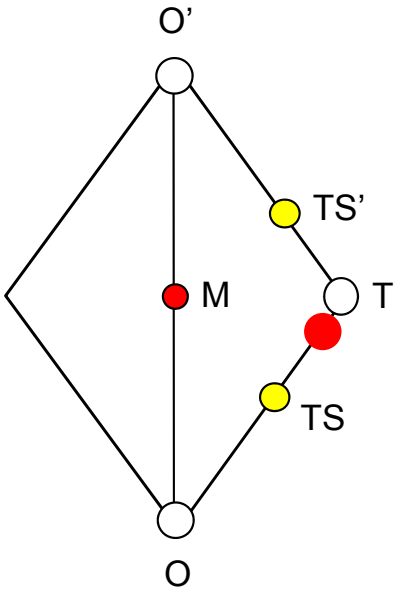

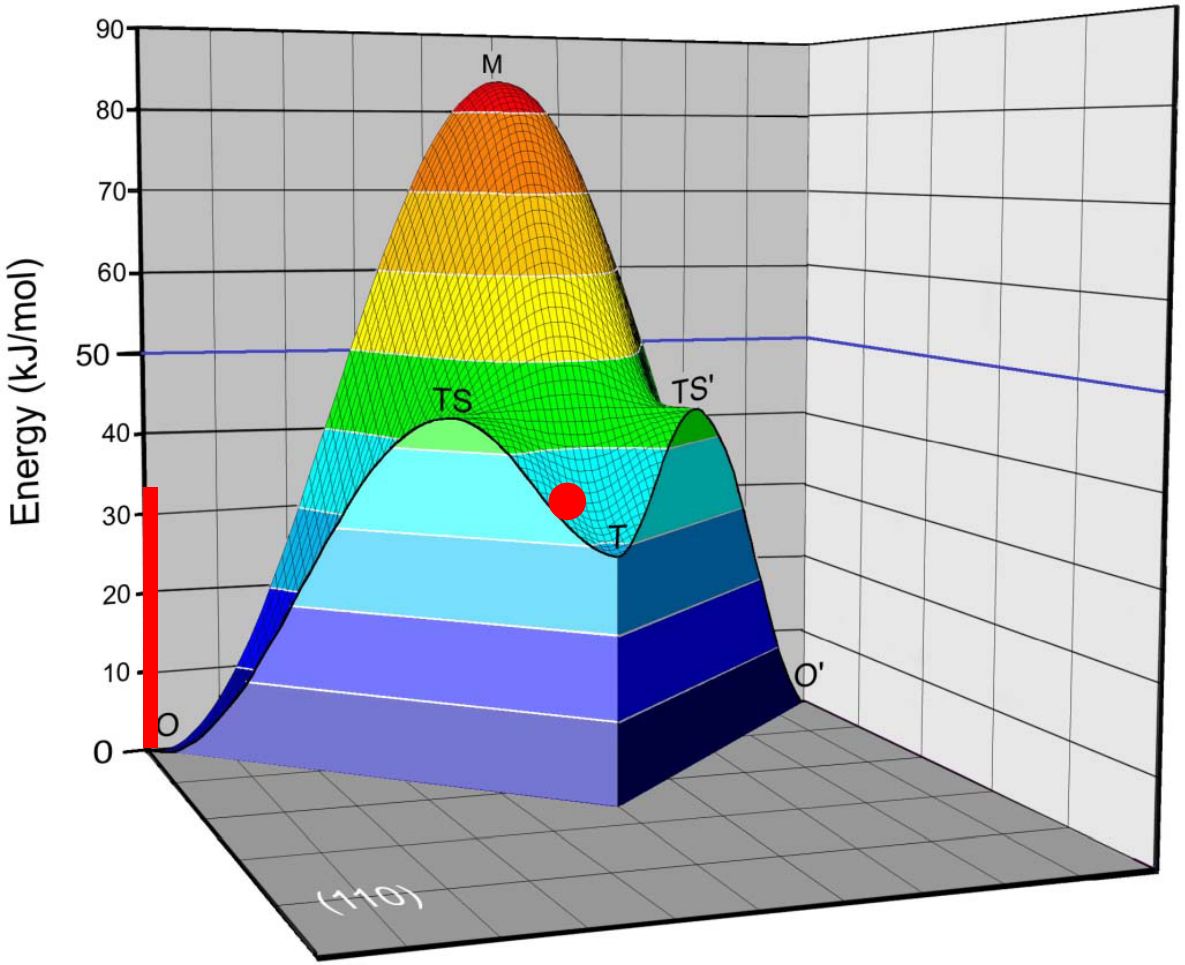

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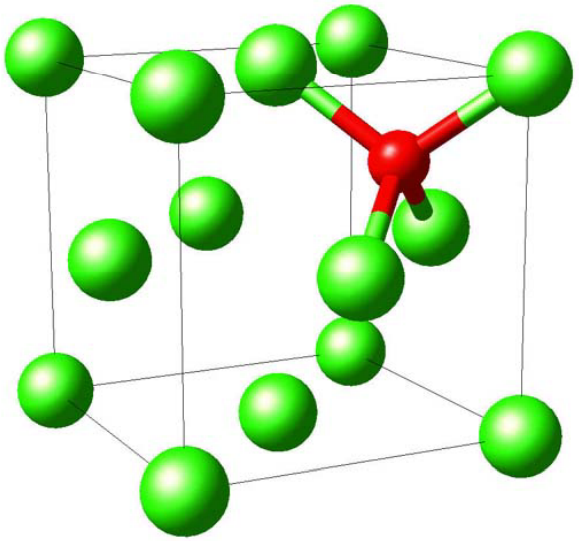

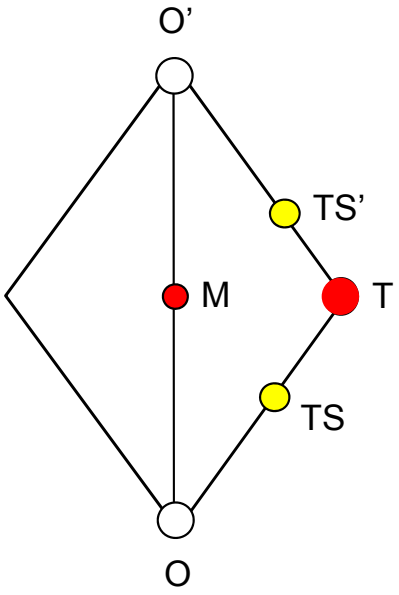

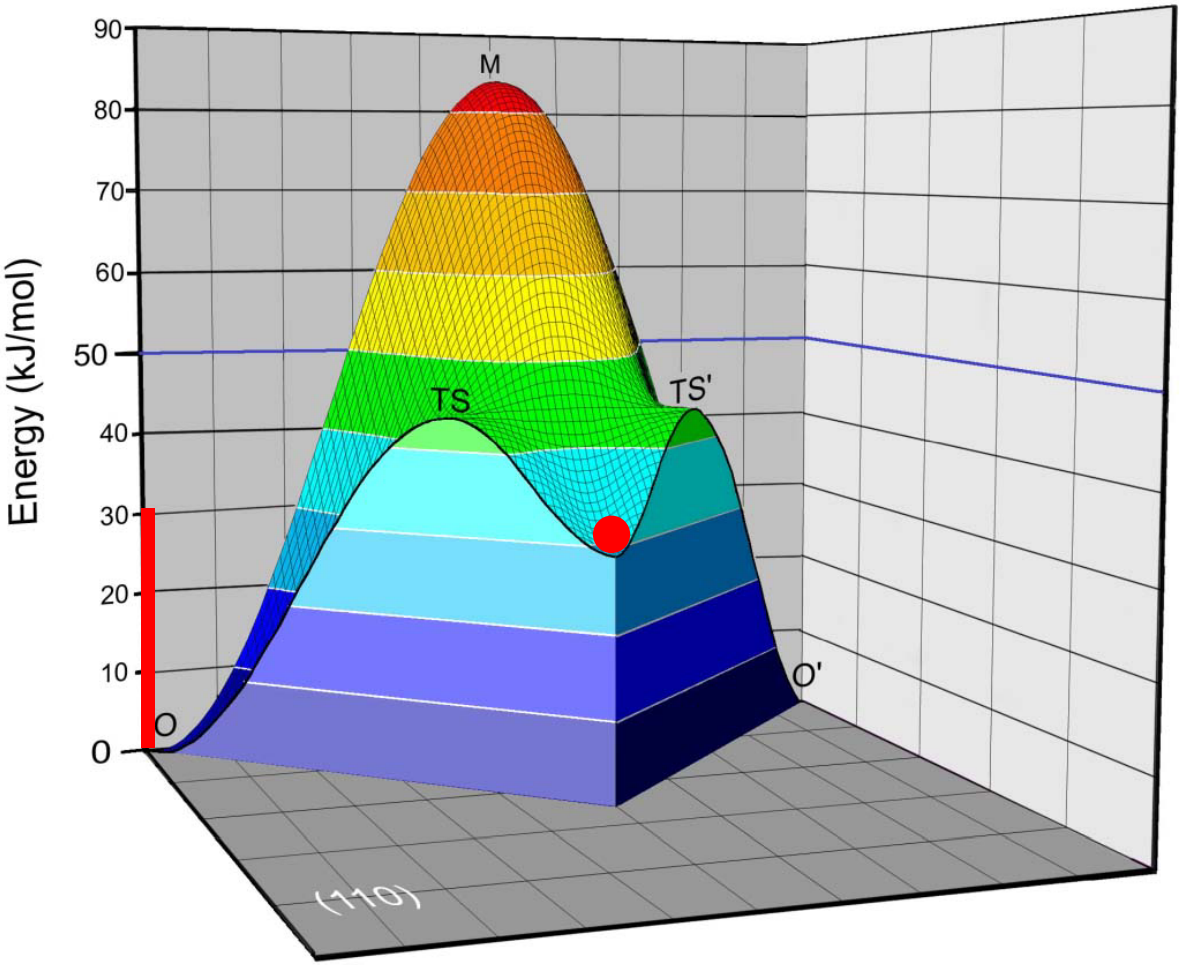

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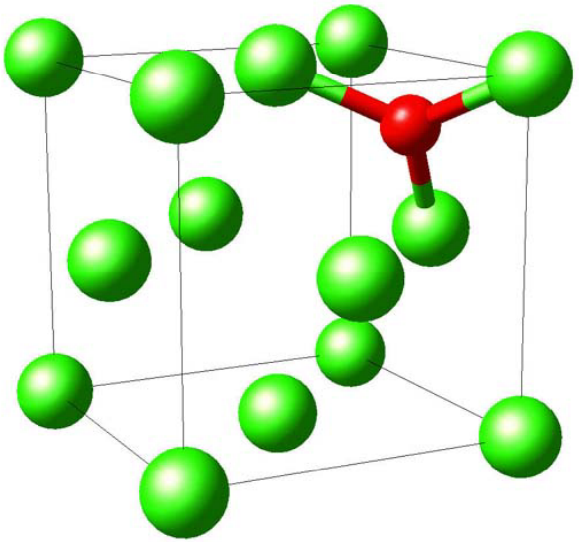

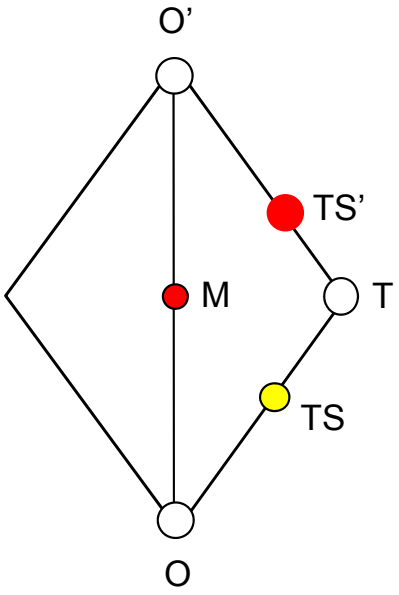

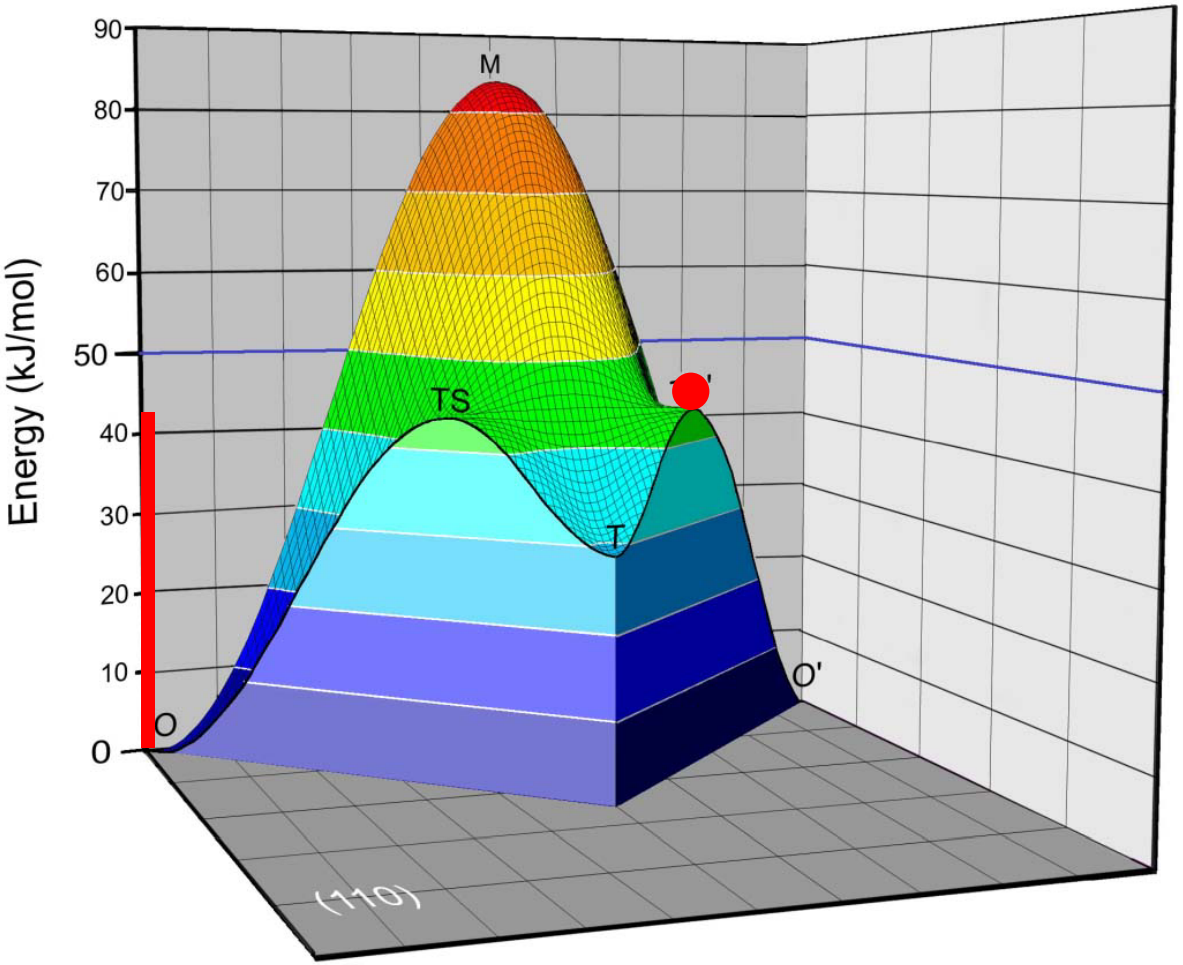

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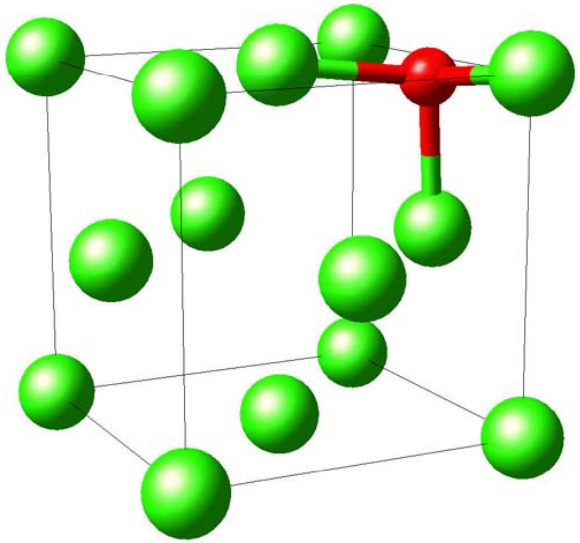

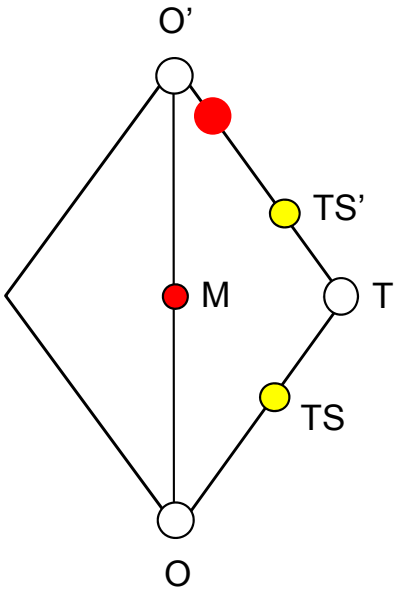

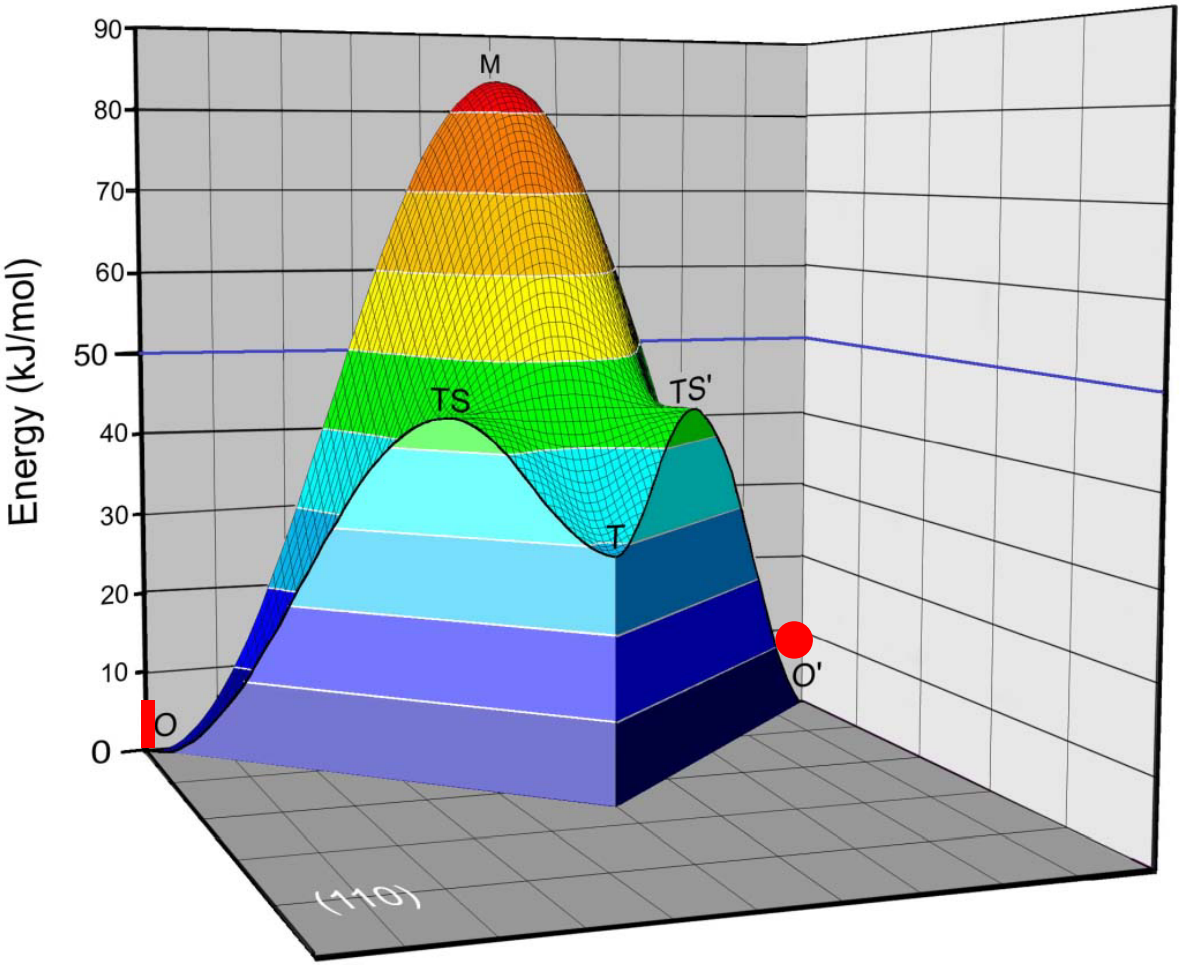

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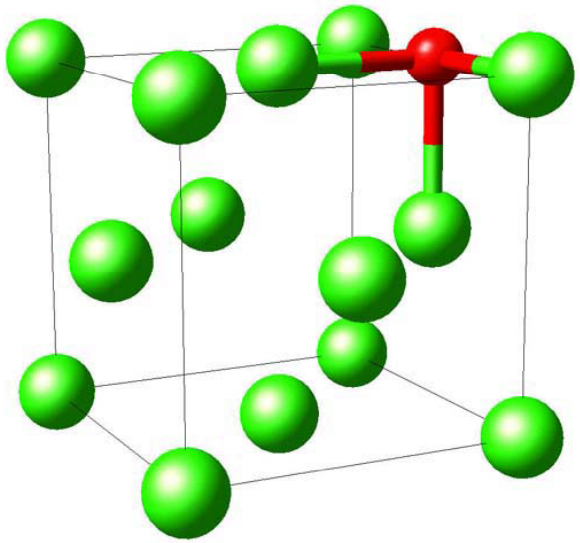
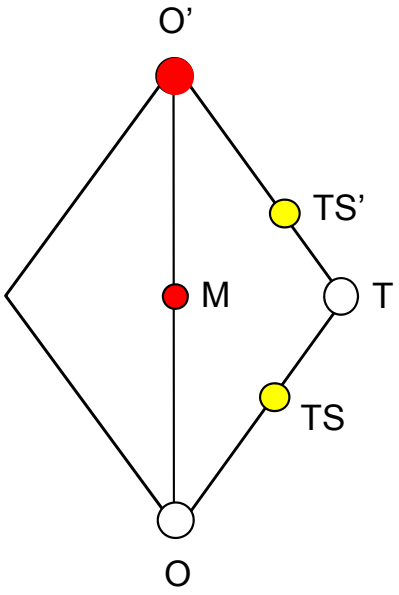
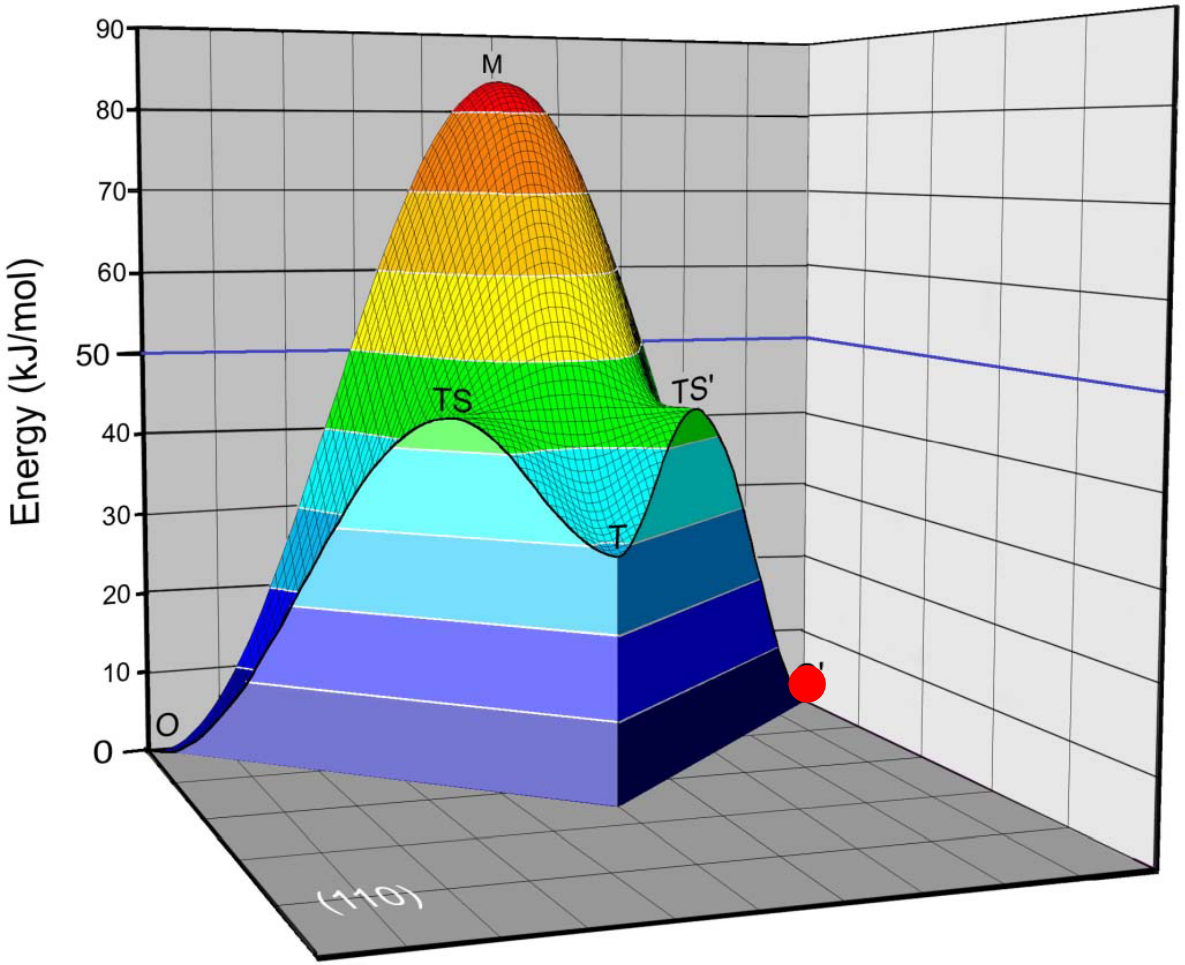
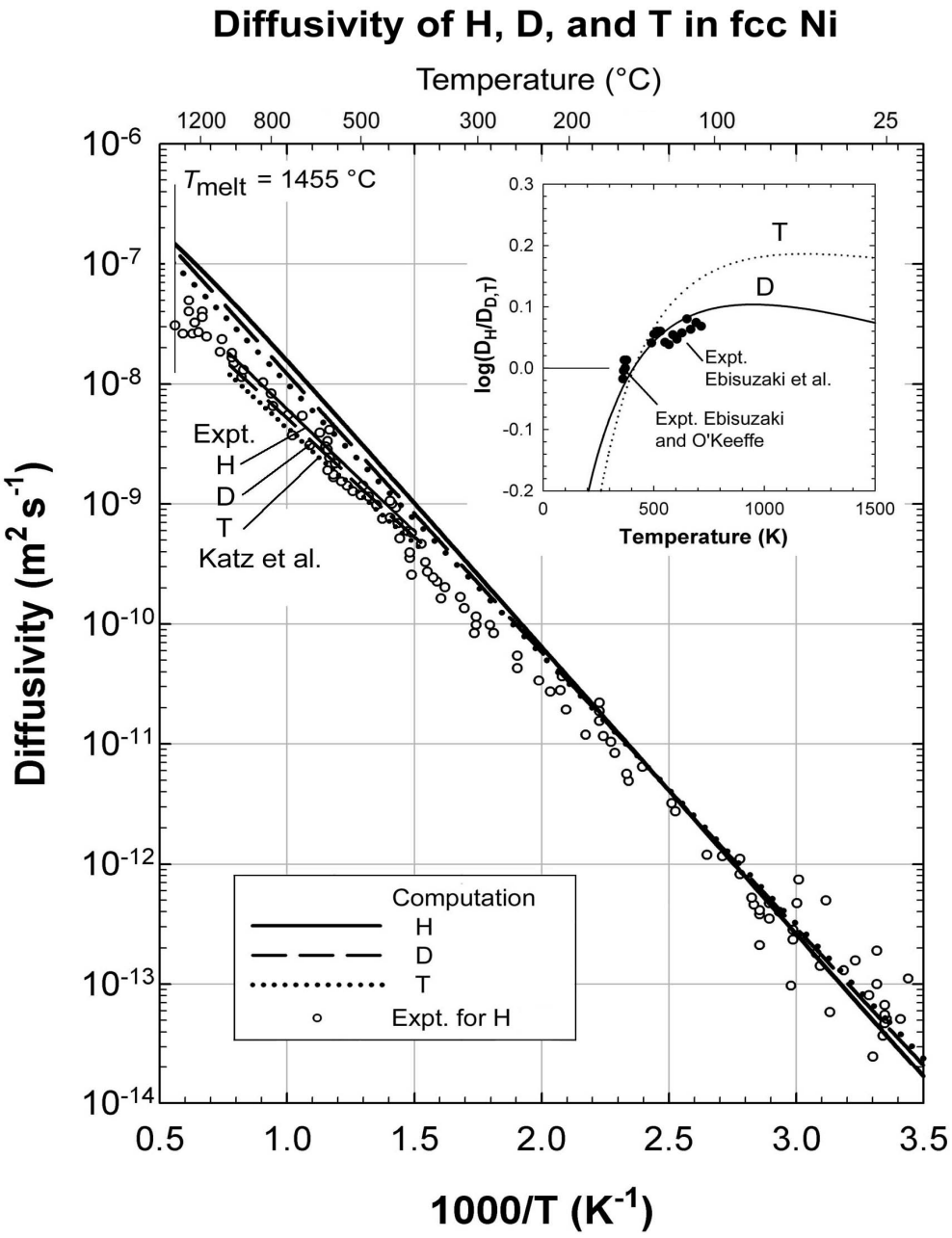






Benchmark Hydrogen in Ni

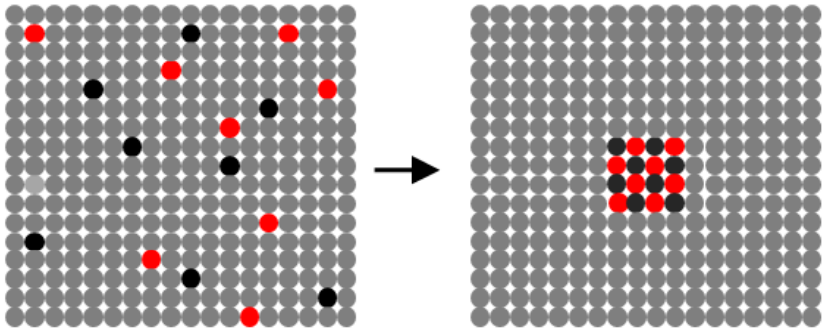


The diffusion coefficient of H in Ni computed from first-principles has similar accuracy as experimental data at ambient and medium temperatures

Isotope effects are well explained and quantitatively described

E. Wimmer, W. Wolf, J. Sticht, P. Saxe, C. B. Geller, R. Najafabadi, and G. A. Young, "Temperature-dependent diffusion coefficients from *ab initio* computations: Hydrogen, deuterium, and tritium in nickel", Phys. Rev. B **77**, 134305 (2008)

Validation: Solubility



$$MX_{solid} \rightleftharpoons M_{maxtrix} + X_{matrix}$$

$$K_{eq} = [M][X]$$

$$K_{eq} = \exp\left(\frac{-\Delta G}{RT}\right)$$

Equilibrium constant

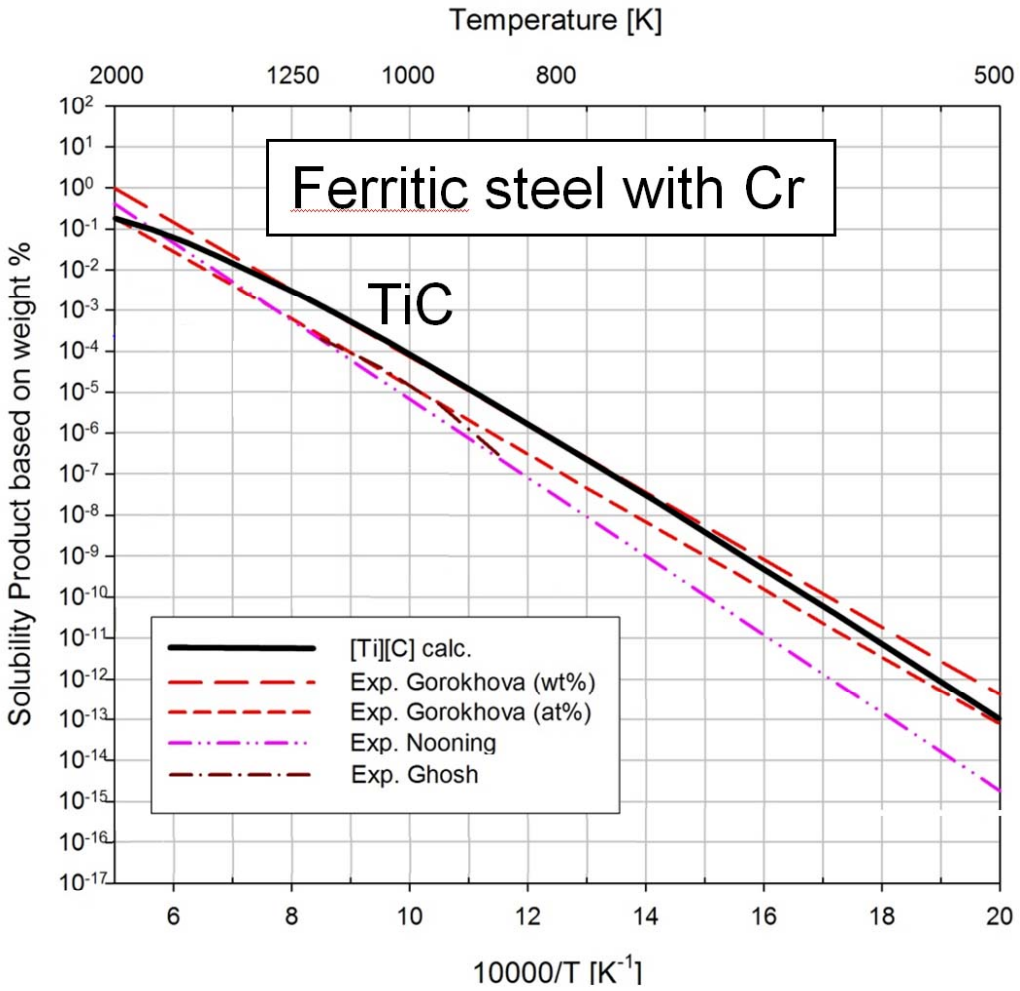
Solubility product $[M][X] = \exp\left(\frac{-\Delta G}{RT}\right)$

At 500 K an error of 10 kJ/mol in ΔG results in an error of about a factor of 10 in the solubility product

Typically reported as logarithmic plot

$$\log[M][X] = A - \frac{H}{T}$$

Computed vs. Experimental Solubility Product



$$\log[M][X] = A - \frac{H}{T}$$

- Computed solubility product of TiC in ferritic Fe-Cr steel is similar to available experimental data
- Accurate electronic energies, inclusion of vibrational entropy (full phonon spectra) and thermal expansion are critical
- Ab initio calculations provide quantitative materials property data for alloy engineering

Wolf et al. (unpublished)

Perspectives

- Ab initio simulations are a necessary part of life time predictions for slow low temperature phase changes
- Examples
  - Ordering and phase segregation in Ni-Cr alloys
  - Diffusion
  - $\alpha+\alpha'$ decomposition
  - Solubility products
- Integration with microstructure and macroscopic simulations methods
- “So much to do, so little done”

Backup