

First Principles Contributions to the Thermodynamic Assessment of Solid State Metal Hydride and Complex Hydride Phases

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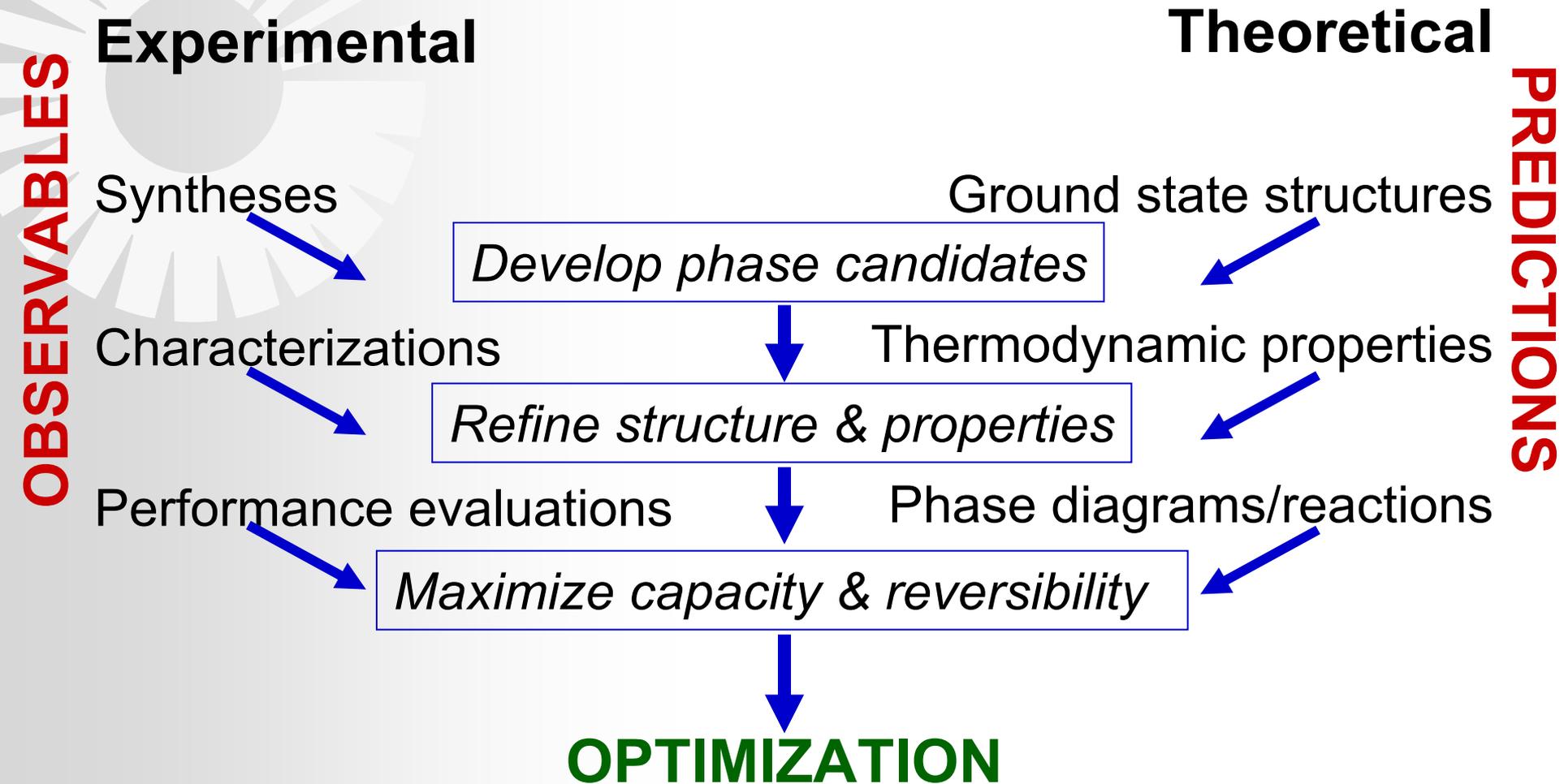
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Rationale for H Storage Media Development



US DOE 2010 Target = 6.0 wt. % H₂ Storage System

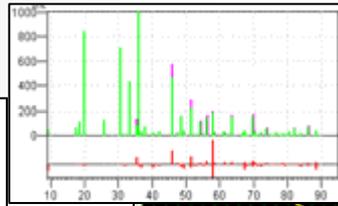
Optimization through parallel implementation of experiment and theory.

Coupled Modeling Methodologies

JADE



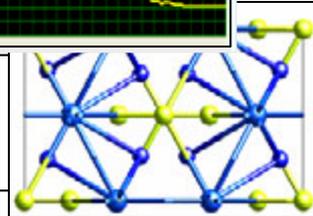
Crystal Indexing
Global Optimization



Crystallographic
Refinement



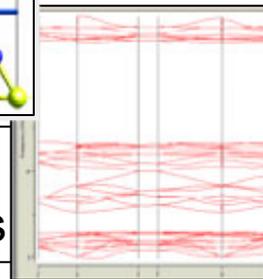
Density Functional Theory
Ground State Minimization



Thermodynamic
Database Building



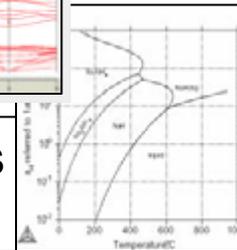
Direct Method Lattice Dynamics
Finite T Thermodynamic Predictions



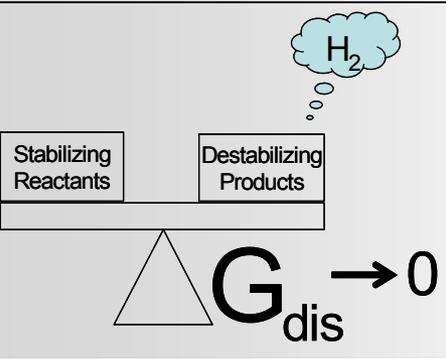
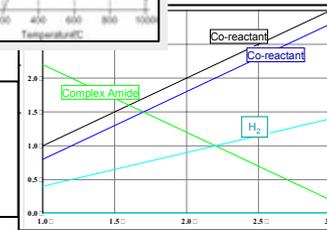
Experimental
Guidance



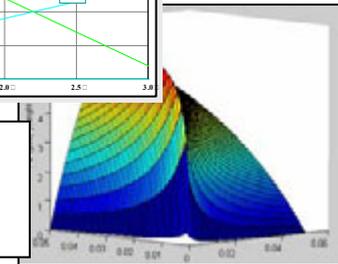
Computational Thermodynamics
Assessment & Phase Diagrams



Thermochemistry
Design of Reversible Reactions



Thermodynamic Optimization
of Theoretical H Capacity



Repertoire of methodologies for virtual discovery & design of high H capacity systems.

First Principles Density Functional Theory

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho(\mathbf{r})]$$

Kohn-Sham Equation

VASP (Vienna Ab Initio Simulation Package)

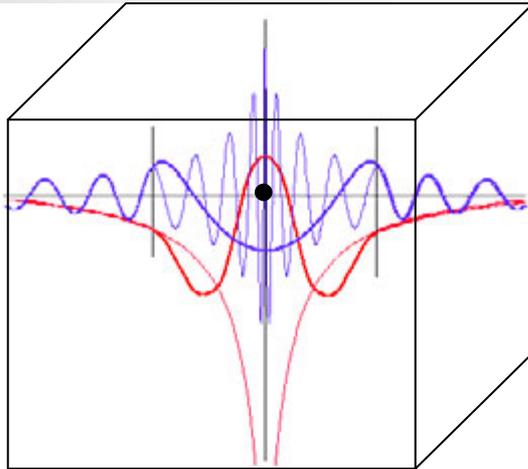


Illustration: D.R.Bowle (1997)

Periodic, plane wave,
PAW potential method

- All Electron Potential
- Pseudo-Potential
- All Electron Wavefunction
- Pseudo-Wavefunction

GROUND STATE MINIMUM

- Ionic Structure
- Density of Electronic States
- Charge Distribution

MEDEA PHONON

- Lattice dynamics including
Finite T thermodynamics
IR and RAMAN activities

Parlinski Direct Method Lattice Dynamics

Implemented in Materials Design Phonon Module:
Calculate forces from atomic displacements in supercell.

$$\Phi_{i,j}(n, \mu; m, \nu) = \left[\frac{\partial^2 E}{\partial R_i(n, \mu) \partial R_j(m, \nu)} \right] \quad \text{Force constant matrix}$$

$$F_i(n, \mu) = \sum_{m, \nu, j} \Phi_{i,j}(n, \mu; m, \nu) U_j(m, \nu) \quad \text{Force due to atomic displacement } U_j$$

Determine dynamical matrix, and phonon frequencies.

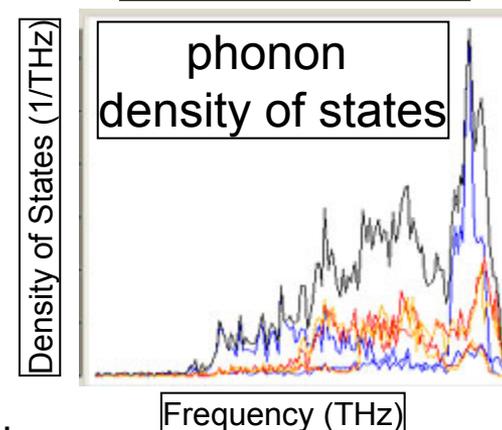
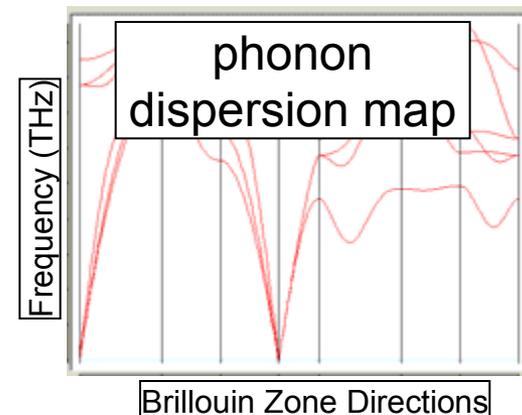
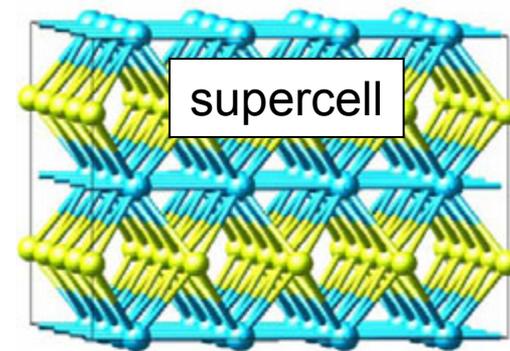
$$D(k; \mu, \nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_m \Phi(0, \mu; m, \nu) e^{2\pi i k \cdot [R(0, \mu) - R(m, \nu)]} \quad \text{Fourier transform}$$

$$D(k) \cdot e(k, j) = \omega^2(k, j) e(k, j) \quad \text{Equation of motion}$$

$\omega^2(k, j)$ = phonon frequencies

Integrate phonon DOS to determine thermodynamics.

$$g(\omega) = \frac{1}{nd\Delta\omega} \sum_{k,j} \delta_{\Delta\omega}(\omega - \omega(k, j)) \quad \text{Frequency distribution over normal modes}$$



Thermodynamics by Phonon Direct Method

Applications:

Solid-state periodic crystalline materials

- stable phase allotropes
- fixed stoichiometry and atomic configuration
- fully minimized ground state structures

Gaseous states

- from sum vibrational frequencies at Γ point only
- need to include PV, translational, and rotational depending on nature of species

Assumptions:

- Supercell larger than interaction range of constituent atoms
- Harmonic – up to quadratic order terms in displacements only

Extensions:

- Zero point energy expansion
- Thermal expansion or other changes with T
- LO/TO Zone Center Splitting

Finite T Thermodynamic Predictions

The total Gibbs free energy of a stoichiometric compound is determined as:

$$G(T) = E_{\text{elect}}(0 \text{ K}) + E_{\text{vib}}(T) + E_{\text{trans}}(T) + E_{\text{rot}}(T) + PV - S_{\text{vib}}(T)$$

The $E_{\text{elect}}(T)$ is approximated by the VASP DFT $E_{\text{elect}}(0 \text{ K})$ calculation. Changes in $E_{\text{elect}}(T)$ with temperature are insignificant at low temperature.

The $E_{\text{vib}}(T)$ and $S_{\text{vib}}(T)$ are derived from integrated phonon DOS:

$$E_{\text{vib}}(T) = \sum_{i,\mu} E_{i,\mu} \quad E_{i,\mu} = \frac{1}{2} d \int_0^{\infty} g_{i,\mu}(\omega) \hbar \omega \coth\left(\frac{\hbar \omega}{2k_B T}\right) d\omega$$

$$S_{\text{vib}}(T) = \sum_{i,\mu} S_{i,\mu} \quad S_{i,\mu} = dk_B \int_0^{\infty} g_{i,\mu}(\omega) \left\{ \left(\frac{\hbar \omega}{2k_B T} \left[\coth\left(\frac{\hbar \omega}{2k_B T}\right) - 1 \right] \right) - \ln \left[1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right) \right] \right\} d\omega$$

$E_{\text{vib}}(T)$ includes zero point energy $E_{\text{vib}}(0 \text{ K})$ and the $E_{\text{vib}}(T) - E_{\text{vib}}(0 \text{ K})$ contributions. The PV, $E_{\text{trans}}(T)$ and $E_{\text{rot}}(T)$ contributions are important mainly for gases.

Error in Finite T Predictions

Typical error estimated to be 5 -15 kJ/mol FU. Error mainly originates from the exchange-correlation approximation in electronic energy determination.

Error contributions due to volume T dependency and electric field polarization are secondary (generally $\ll 1$ kJ/Mol FU). Determinations of quasiharmonic approximation and Born effective charges are computationally intensive.

Vibrational contributions are dependent on the shape of the potential energy surface, not its absolute position. Systematic errors tend to cancel.

Exchange-correlation is being addressed in new code development:

- Hybrid functionals, as well as schemes like screened exchange.
- Accuracy in total energies and geometries will improve somewhat.
- Computational cost will be higher (possibly up to 50-100X).

Introduction to CALPHAD Methodology

CALPHAD “CALculation of PHAse Diagrams”

Thermodynamic description of phases within a system enabling modeling of:

- transformations and property evolution during processing or use
- phase diagrams for a range of conditions

Descriptions are typically developed sequentially for contributing systems of increasing order (no. of elements). Several lower order descriptions may be extrapolated to describe higher order systems, to a limited extent.

Traditionally, the descriptions are developed from assessments, involving the development of models, selection and fitting of experimental data. Parameters are derived from the refinement of simultaneous fits, i.e. for the empirical $G(T)$ expression for a known compound:

$$G_m = a + bT + cT \ln(T) + dT^2 + eT^3 + \dots + f / T$$

These parameters are then evaluated by comparing modeling with measured values that were not included in the assessment.

Implementation of CALPHAD Methodology

Other thermodynamic properties can be derived from the empirical Gibbs free energy polynomial equation:

$$G_m = a + bT + cT \ln(T) + dT^2 + eT^3 + \dots + f / T$$

using standard thermodynamic relations, such as:

$$H_m = \partial(G_m / T) / \partial(1/T) = a - cT - dT^2 - 2eT^3 + \dots + 2f / T$$

$$S_m = \partial G_m / \partial T = -b - c(1 + \ln T) - 2dT^2 - 3eT^3 + \dots + f / T^2$$

$$C_p = \partial H_m / \partial T = -c - 2dT - 6eT^3 + \dots - 2f / T^2$$

For inorganic hydrides, the polynomial parameters are typically derived from fits to the following measured physical properties :

Enthalpy of Formation can be used to determine a

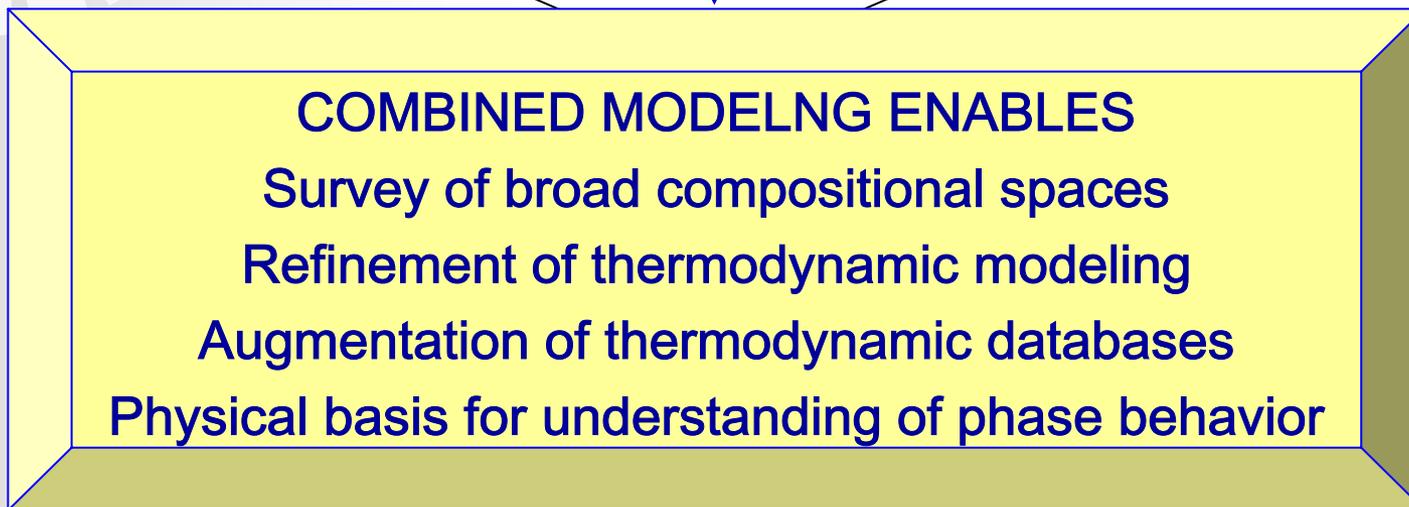
Dissociation pressure data can be used to determine a and b

Heat capacity data can be used to determine c, d, e, f

Leveraging of Modeling Methodologies

- simulate unknown and/or uncharacterized compounds
- virtual investigation preceding compound discovery
- results subject to experimental validation

First Principles Modeling



Thermodynamics

- simulate multi-order phase behavior
- reliability dependent on data accuracy and integrity
- only predicts stability of phases included in database

Integration of Experiment and Predictions

First principles calculations can also predict known compound properties for conditions that are difficult or impossible to measure in the laboratory:

- 1) Extreme temperature and pressure conditions
 - provides a physical foundation for extended modeling range
- 2) Standard state free energies of formation
 - may be difficult to measure directly
 - eliminates need for Neumann-Kopp rule
- 3) Lattice stabilities for elements or compounds
 - allotropes unstable under given conditions (ie. low T)
 - can reduce number of parameter fits in assessments
- 4) Hypothetical end-members $G_{i_i}^o$ and mixing behavior G_m^{ex}
 - fully substituted sublattice or interstitial lattice
 - eliminates need to estimate or fit parameter

empirical substitutional
solution equation

$$G_m = \sum y_i G_{i_i}^o + RT \sum y_i \ln y_i + G_m^{ex}$$

Conclusions



- * Coupled first principles-experimental-thermodynamic methodologies provide a foundation for refining phase structures, enhancing thermodynamic databases, and guiding development of new compounds.
- * Direct method lattice dynamic and thermodynamic predictions are valuable for assessing compound structures and surveying reaction mechanisms.
- * Direct method finite T thermodynamic predictions are complementary to measured data and should be assessed prior to inclusion into databases.
- * The inherent inaccuracy in DFT is often commensurate with that observed between different experiments. Improvements are forthcoming.