Thermodynamic Assessment of Cr-Ni Based on the Third-generation Unary Data and Improved Magnetic Model

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Introduction

In order to promote the reliability and applicability of the CALPHAD approach, the third-generation thermodynamic database based on physical models is being developed. As a case study, this work re-optimize the binary Cr-Ni system using the third-generation Gibbs free energy functions of Cr and Ni, along with the Inden-Hillert-Xiong (IHX)'s magnetic model [1]. Compared with the second-generation unary database [2], the third-generation data are valid down to 0 K and avoid unphysical kinks around the melting point. Meanwhile, the predicted magnetic properties by the IHX model are in better agreement with experimental measurements or theoretical calculations than the Inden-Hillert-Jarl (IHJ) model [3].

Motivation

The second-generation thermodynamic models have some limitations:

- Invalid at temperatures lower than 298.15 K
- Discontinuous around the melting point of pure elements
- Unreliable when predicting magnetic properties for a system composed of elements with incommensurate magnetic states

There is a critical need to develop the third-generation, physics-based CALPHAD models to render reliable predictions for low-temperature thermodynamics and magnetic properties.

Models and Approach

Physics-based model [4] for heat capacity of elements

Solid Phase

$$C_p = 3R\left(\frac{\theta_E}{T}\right)^2\frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2} + aT + bT^n + C_p^{mag}$$

- Harmonic lattice vibration
- Electronic excitation + low-order anharmonic correction
- High-order anharmonic lattice vibration

Liquid Phase

$$G^{liq-am} = G\left(\frac{\theta_E^{am}}{T}\right) + D + ET^2 - RTln[1+\exp(-\Delta G_d/RT)]$$

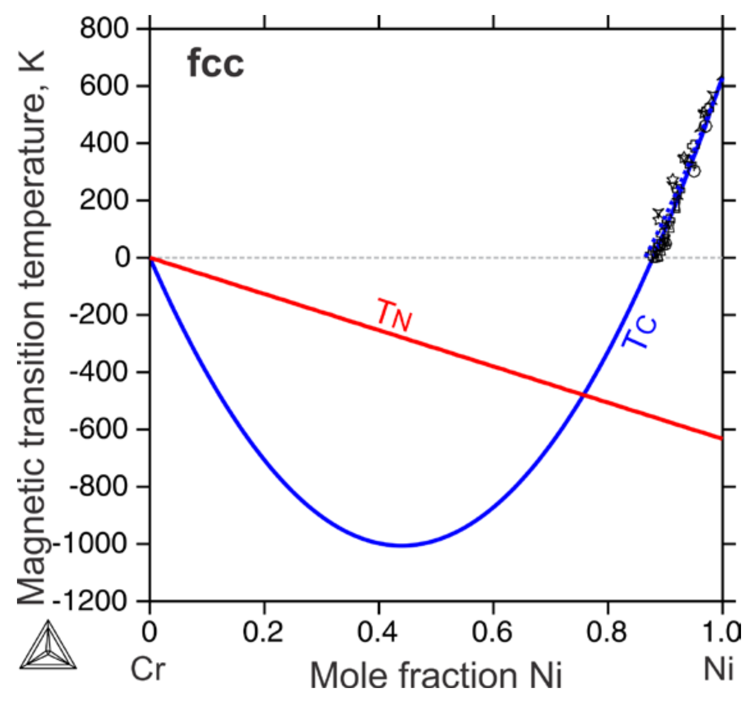
- Gibbs free energy of the amorphous-like state
- Gibbs free energy difference between liquid-like and amorphous-like states $\Delta G_d = A + BT + CTlnT + \cdots$

Impose constraints on extrapolation Gibbs free energy function [4]

$$G = G\left(\frac{\theta_E}{T}\right) + H' - S'T + a'T(1-lnT) - \frac{b'}{30}T^{-5} - \frac{c'}{132}T^{-11} + G^{mag} \quad (T > T_m)$$

Make sure the **enthalpy**, **entropy**, **heat capacity**, and the **first derivative of heat capacity** are continuous at the melting point.

IHX model for magnetic properties prediction



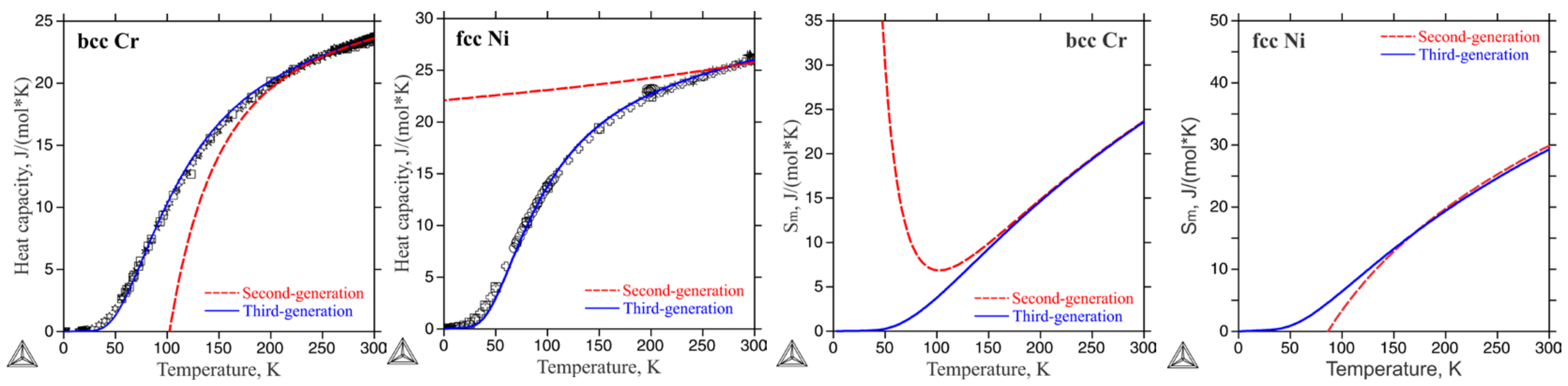
- Two Redlich-Kister polynomials are used to calculate the Curie and Néel temperatures of a magnetic solution phase independently
- To include local magnetic states, **effective magnetic moment** is used to calculate the magnetic ordering energy

$$\beta = \prod_i (\beta_i + 1)^{x_i} - 1$$

β_i: Local magnetic moment of atom i

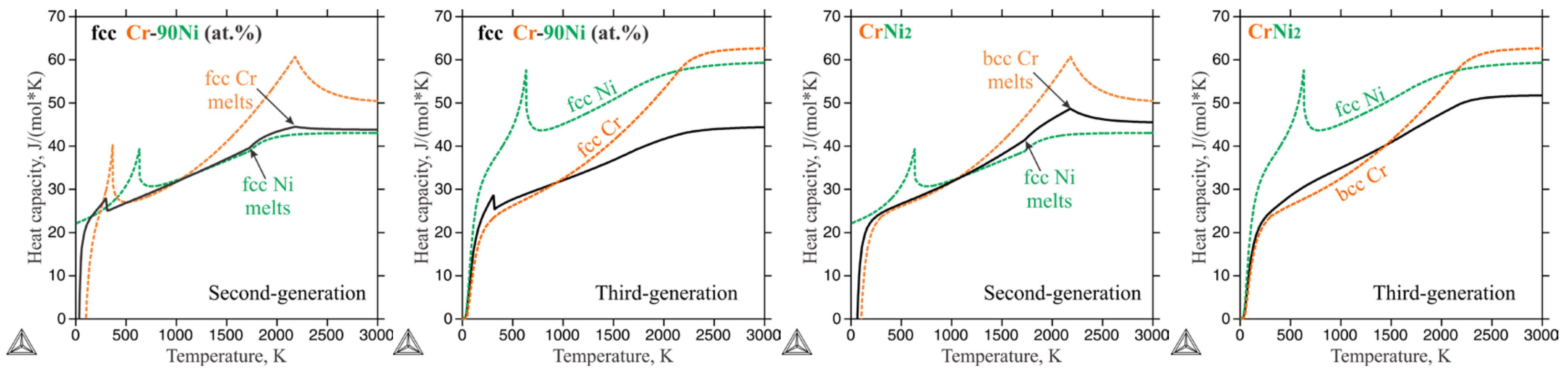
Results

Thermodynamic predictions are valid down to 0 K



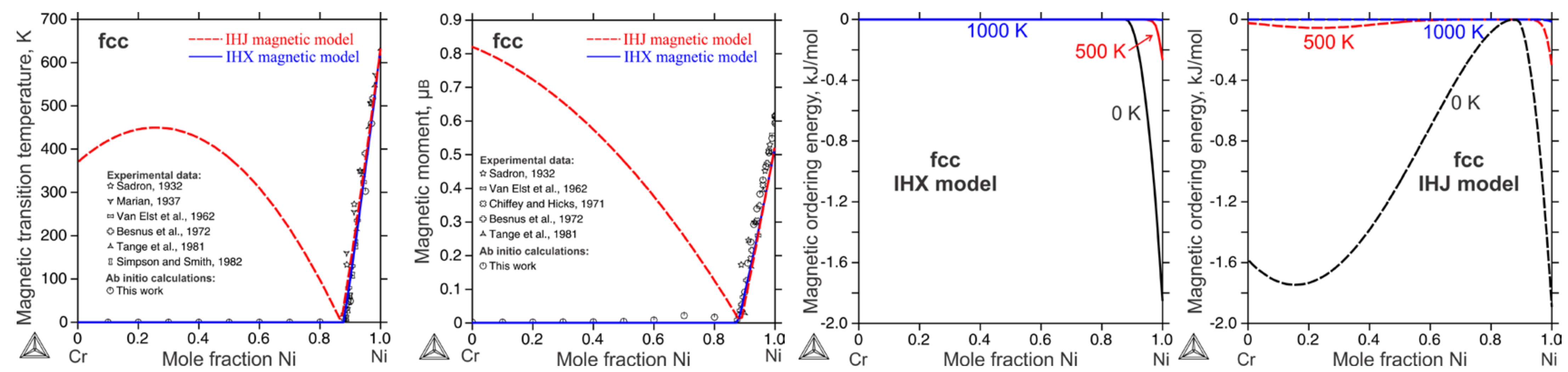
- Predicted **low-temperature heat capacity** fits well with experiments
- Predicted **entropy** is zero at 0 K for solid structures

Thermodynamic properties are continuous over the whole temperature range



- For both the solution and the intermediate phases, **unphysical kinks** due to melting of elements are removed

Predicted magnetic properties can reproduce experimental/theoretical results



- **Magnetic properties** are accurately predicted for elements with **different magnetism**
- **Magnetic contribution to Gibbs free energy** is reasonably calculated

Conclusions

- Based on physical models for heat capacity, the third-generation unary data is suitable for low-temperature thermodynamics prediction.
- Unphysical kinks appearing when pure elements melt are removed by constraints applied to the Gibbs energy function above the melting point.
- The IHX magnetic model avoids artificial magnetism in the magnetic phase diagrams and thus reasonably predicts the magnetic ordering energy.

References

[1] W. Xiong et al., Calphad, 39 (2012) 11–20.
[2] A.T. Dinsdale, Calphad, 15 (1991) 317–425.
[3] M. Hillert et al., Calphad, 2 (1978) 227–238.
[4] Q. Chen et al., J. Phase Equilibria, 22 (2001) 631–644.

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