

Title	磁石合金の状態図計算に対する第一原理アセスメント
Author(s)	HANINDRIYO, Adie Tri
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Description	Supervisor:前園 涼, 先端科学技術研究科, 博士

# Abstract

As a highly important system both in the academic and the industrial world, there is great interest in information surrounding the Nd-Fe-B ternary system. Its importance is largely derived from one of its ternary phase, the  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , which is used as the base compound for the most powerful permanent magnet materials available today. Alloying  $\text{Nd}_2\text{Fe}_{14}\text{B}$  with other elements (substitution in atomic sites) has long been a reliable method to engineer material properties suitable for various uses. A famous example is the  $\text{Nd}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$  compound, which substitutes several iron (Fe) sites with cobalt (Co) in order to increase the Curie temperature ( $T_C$ ), effectively increasing the working temperature of the resulting permanent magnet. Another would be the substitution of neodymium (Nd) sites with dysprosium (Dy) in order to raise the coercivity, or resistance to demagnetization by an external opposing magnetic field. Such efforts have largely produced the types of permanent magnet materials currently used in academic and industrial instruments.

Issues concerning the phase stability often arise when atomic substitution is performed, since substitution involves introducing stress and strain to the atomic crystal structure of an otherwise stable phase. Often, atomic substitution results in symmetry breaking, additional charges, and most severely destabilization of the phase. It is imperative therefore that full information regarding phase stability is obtained prior to organizing atomic substitution. Phase diagrams, therefore, are indispensable to this endeavor, and as such the CALPHAD (Calculation of PHase Diagrams) method of computational thermodynamics is highly relevant as a computational framework to draw these diagrams. The core of the CALPHAD framework is the modelling of Gibbs energy models of the competing phases in a system in order to reliably model phase transitions occurring under certain conditions (pressure, temperature, composition, *etc.*), in order to draw the phase diagram as a function of these conditions. In this work the temperature  $T$  and composition  $x$  are taken as the two degrees of freedom for the phase diagrams.

In order to ensure reliability of the models, parameters are built in to the Gibbs energy models used in CALPHAD in order to perform fitting to actual thermodynamic data of constituent phases within a system. This ensures that the resulting modes accurately represent the phase stability of the competing phases, leading to a more accurate and reliable prediction of phase transitions. The data used for the fitting process has traditionally been obtained from experimental studies; however, while previous assessments of the Nd-Fe-B ternary system exist, the lack of experimental data regarding constituent phases of the Nd-Fe-B system has hampered the effort so far. In this work, we introduce *ab initio* predictions of thermodynamic properties of Nd-Fe-B to the CALPHAD assessment of the binary Nd-B system, one of the constituent systems in the Nd-Fe-B ternary system, which within the CALPHAD framework is necessary in order to investigate the ternary system as a whole.

Therefore, *ab initio* calculations of thermodynamic properties of compounds in the Nd-Fe-B ternary system and the Fe-B, Nd-B, and Nd-Fe binary systems are required to provide more complete information for CALPHAD assessment of the ternary system. The Fe-B binary system, being relatively well-investigated (due to its role in the steel industry), is excluded from the scope of this work. Two thermodynamic properties, the enthalpy of formation and the specific heat in constant pressure ( $C_p$ ), are particularly relevant in the investigation, for the fitting of Gibbs energy models in CALPHAD. Density Functional Theory (DFT), as well as phonon calculation, are used as *ab initio* investigation methods to obtain the two properties for a variety of Nd-Fe-B constituent phases.

These calculations have been performed for the compounds  $\text{NdB}_6$ ,  $\text{NdB}_4$ ,  $\text{Nd}_2\text{B}_5$ ,  $\text{Nd}_2\text{Fe}_{17}$  and  $\text{Nd}_5\text{Fe}_2\text{B}_6$ . We find that the conventional exchange correlation functional GGA (Generalized Gradient Approximation) in the DFT framework is insufficient to reliably obtain the enthalpy of formation for rare earth compounds. Instead, the Hubbard U correction based on the framework of Cococcioni and de Gironcoli (DFT+U) is employed, with values of the correction parameter  $U_{\text{eff}}$  determined from *ab initio* as well. The enthalpy of formation values obtained with the GGA+U correction shows better agreement with the available experimental data than the non-corrected GGA. We have also computed the vibrational and electronic contribution to the heat capacity ( $C_p$ ) of the compounds as a function of temperature from  $0 < T < 3000$  K. The results are fitted as a sum of functions from  $300 < T < 3000$  K. Both the enthalpies of formation and  $C_p$  data have been utilized to reoptimize the Gibbs energy models for the binary Nd-B system, leading to a reoptimized phase diagram of the system.

Keywords: CALPHAD, *ab initio*, Nd-Fe-B, permanent magnets, phase diagram