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論文の内容の要旨

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 NdB₆, NdB₄, Nd₂B₅, Nd₂Fe₁₇ and Nd₅Fe₂B₆. 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_{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*

論文審査の結果の要旨

ネオジウム磁石合金に元素置換などを施して有用な物性の調整を図る材料開発が繰り返されている。こうした材料開発において、元素置換された組成比においてどのような安定相が実現されるかを知ることは最基礎の情報に相当し、その知見は「合金系の状態図」として提供される。ネオジウム合金の状態図を明らかにすることは、したがって、国際的にも注目度の高い研究題目となっている。系のギブスエネルギーモデルを与えれば、熱力学理論に基づき演繹的に状態図を導出出来る。このモデルはまた、定圧比熱や生成エンタルピーなど熱力学量を導く。そこでギブスエネルギーモデルを冪展開

などの関数型で表現し、そのパラメタを「実測熱力学量が再現されるようにフィッティングして決定」し、得られたモデルから数値的に状態図を算定する「CALPHAD」という枠組が確立している。ところがネオジム合金に適用する場合、入手できる実測データが少なくモデルを確定することが出来ないという問題がある。それゆえ、当該法の先行研究群では、算定される相境界がばらつき、実用に耐える予測は実現できなかった。第一原理電子状態計算は、近年、実用性を高めつつあり、「CALPHAD によるフィッティング」に必要な各種熱力学量を算定することが可能となってきた。ネオジム合金の第一原理計算で熱力学量を算定できれば、CALPHAD による状態図予測に繋ぐ「第一原理アセスメント」が原理的には可能である。しかしながら、*d*電子/*f*電子のもつ局在性に起因した「多体電子相互作用記述の大きな困難」があり、その第一原理アセスメントは未踏であった。本論文は、これを初めて手掛けた業績であり、第一原理計算で補完された十分なデータ点数を以て、相境界に不定性の少ない状態図をはじめ提供した。上記の多体電子相互作用に対しては、「DFT+U 法」の適用が必須であること、および、その効用はエンタルピー寄与に対して顕著で、エントロピー寄与にはあまり影響を与えないことなど、数々の基礎的知見を見出し、その研究成果の一部は既に、申請者を主著者とする査読付原著論文成果[A. T. Hanindriyo et al., *Comp. Mater. Sci.* 180, 109696 (2020/IF=2.644)]に発表され、当該コミュニティにおいて一定の評価を獲得している。

以上、本学位論文は、第一原理計算の援用が期待されながらも、基礎理論的な困難故に他者が到達しえなかった「磁石合金の状態図予測」をはじめ実現したというインパクトの高い業績と言える。また、明らかにされた基礎的知見と確立されたスキームは「*d*電子/*f*電子の局在性」を内在する磁石合金全般に広く適用可能な有用なものであり、よって重要な業績として学術的に貢献するところを認め、よって博士(マテリアルサイエンス)の学位論文として十分価値あるものと判断した。