First-principles Study of Thermodynamic Stability in Multi-elements Alloying $(Sm,X)(Fe,Y)_{12}Z$ Compounds

Saengdeejing Arkapol, Chen Ying
(School of engineering, Tohoku University)

$SmFe_{12}$-based compounds have been considered one of the most promising candidates for the next generation high performance magnetic materials. $SmFe_{12}$-based compounds exhibit excellent intrinsic hard magnetic properties with lesser amount of rare earth elements compare to other hard magnetic materials, while synthesizing $SmFe_{12}$ compounds faces a big difficulty due to the thermodynamic stability of these compounds. Additional elements doping has been attempted to stabilize $SmFe_{12}$ compounds. Ti is currently one of the best elements to thermodynamically stabilize $SmFe_{12}$ compounds but it degrades the magnetic properties. Multi-element alloying approach is generally required to achieve the desired stability while minimized the degradation of the magnetic properties. In order to understand the effect of multi-elements on the stability and magnetic properties of $SmFe_{12}$-based compounds with multi-element alloying, systematical calculations of $(Sm,X)(Fe,Y)_{12}Z$ (X=Zr/Ce, Y=Co/V/Ti, Z=B) have been conducted.

The first-principles calculations become increasingly difficult due to the complexity of the structures. The supercell with larger number of atoms to represent the correct composition and random arrangement of atoms becomes inevitable. The Special Quasirandom Structure (SQS) model is adopted to imitate the random atomic configurations. The electronic structure and total energy at 0K are calculated by DFT, the contribution of the lattice vibration at finite temperature to the free energy is obtained from Debye-Grüneisen model[1].

Several SQS for multi-elements alloying in $(Sm,X)(Fe,Y)_{12}Z$ are generated. It is found that all structures are thermodynamically stable with respect to the referent state which is consists of ground state structures of component elements. Equation of state fitting is performed on each SQS to obtain parameters required for Debye-Grüneisen model to evaluate the vibrational free energy. Figure 1 shows the SQS model(a) and calculated free energy as a function of temperature in $Sm(Fe_{0.75}V_{0.25})_{11.5}Ti_{0.5}$ (b), as an example. Different contributions to the free energies are plotted separately to illustrate the magnitude of each contribution to the free energy. It is found that most of 3d transition elements seem to stabilize the $SmFe_{12}$ structure through the vibrational contribution to the free energy in single element doping ($SmFe_{11}Y$). Increasing the concentration of alloying elements beyond $SmFe_{11}Y$ tends to destabilize the structure at the lower temperature. The contributions to the stability of $SmFe_{12}$ compound from the configurational entropy is also important in some systems such as $Sm(Fe_{0.75}Co_{0.25})_{11}V_{0.5}Ti_{0.5}$. By carefully balancing between intrinsic formation energy at 0K, vibrational contribution and configurational entropy, it is possible to design the multi-element alloying $SmFe_{12}$ compound with optimum thermodynamic stability and magnetic properties.

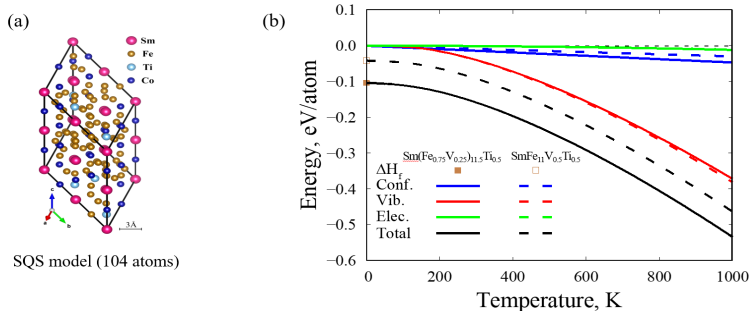

Figure 1: (a)The SQS model for random mixing of Sm $(Fe_{0.75}V_{0.25})_{11.5}Ti_{0.5}$. (b)Free energy at temperature up to 1000K and contributions of each physical effects in $Sm(Fe_{0.75}V_{0.25})_{11.5}Ti_{0.5}$ with comparison to $SmFe_{11}V_{0.5}Ti_{0.5}$.

Reference

1) Moruzzi V.L., et al. *Phys. Rev. B* 37 (1988) 790.