Free-energy evaluation of alloys

Yoshihiro GOHDA
Department of Materials Science and Engineering, Institute of Science Tokyo
J2-22, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8501, Japan

Aiming construction of first-principles phase diagrams, we are trying to develop methods to evaluate free energies of metallic alloys. The free energy is decomposed into a few contributions, including the phonon effects and the configrational entropy as the most important ones. Moreover, other components and couplings among various contributions significantly affects phase equilibria, e.g., phase transition temperatures. Indeed, the spin-phonon coupling changes the Curie temperature of bcc Fe more than 500 K [1].

In this project, we developed a method to perform first-principles phonon calculations to evaluate Gibbs free energies efficiently [2]. In our volume integral of pressure (VIP) method, multiple phonon calculations with varying the volume are avoided in incorporating the effect of thermal expansion. This feature makes the Gibbs-energy evaluation possible for high-temperature austenite phases that is in general difficult for conventional volume-varied approaches, by combining the VIP method with the self-consistent phonon (SCPh) method [3] implementd in the ALAMODE code [4]. In applications to bcc Ti [2], we demonstrated that the electron-phonon coupling changes the austenite-martensite phase-transition tempearature more than 200 K as shown in Fig. 1. We also applied the VIP method to Ti-Al alloys that require huge computational costs.

Conventional CALPHAD approach largely relies on experimental data. In some cases, mixing enthalpies are additionally evaluated from first principles [5]. Evaluation of free energies from first principles should further expand possible range of Gibbs-energy database to experimentally unavailable cases. As one of approaches to achive the goal above, we also developed a method to include the spin-electron coupling in the evaluation of exchange-coupling parameters [6].

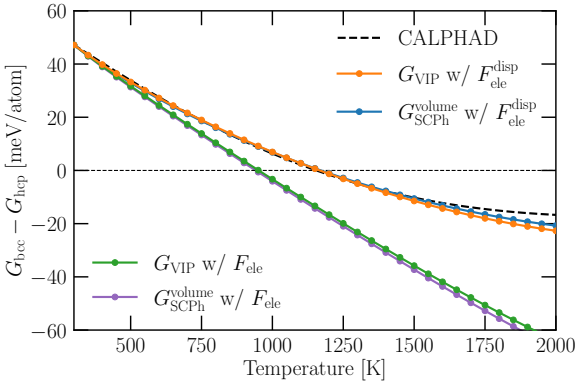

Figure 1: Difference in the Gibbs free energy between bcc and hcp Ti from 300 K to 2000 K. The origin of the DFT calculations is shifted to the CALPHAD data at 300 K, i.e., changes from 300 K are evaluated from first principles. Superscripts "disp" indicate that calculations include the electron-phonon coupling as effects of vibrational atomic displacements.

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