VACANCY CONCENTRATIONS FROM 0K TO THE MELTING TEMPERATURE IN UNARY FCC METALS: DISCOVERY OF LARGE NON-ARRHENIUS EFFECTS

Jörg Neugebauer, Albert Glensk, Blazej Grabowski, Tilmann Hickel

Max-Planck-Institut für Eisenforschung, Düsseldorf

The Gibbs free energy of point defect formation is a critical quantity allowing e.g. to consider such defects in phase diagrams. However, an accurate determination of defect formation energies over the entire temperature window, i.e. from T=0K all the way up to the host melting temperature, is challenging both for experiment and theory. Experimentally, equilibration of point defects is only possible at high temperatures allowing to measure defect concentrations only in a certain temperature window. To extrapolate these high-temperature data to low temperatures commonly an Arrhenius behavior is assumed, i.e., the defect entropy is assumed to be temperature independent. Theoretically, the challenge lies in the various entropic contributions that may become important at high temperatures such as electronic, harmonic and anharmonic excitations and that are computationally extremely expensive. Consequently, in most theoretical studies on point defects only configurational entropy has been considered.

Recent methodological advances provide now the opportunity to compute all these excitation mechanisms with high precision on a fully ab initio basis, making it possible to derive free energies for bulk systems and defects up to the melting temperature. Applying these approaches to vacancies in Al and Cu we were able to derive vacancy formation energies over the entire temperature range. An analysis of these results shows that in particular the inclusion of anharmonic contributions gives rise to a hitherto not expected magnitude of non-Arrhenius effects. We show that the presence of these effects is invisible to conventional experiments measuring vacancy concentrations. Furthermore, we discuss the implications such effects have on enthalpies and entropies of formation. For example, it will be shown that non-Arrhenius effects change defect formation energies by several 0.1 eV. Even more stunning, the defect entropy is found to change by more than an order of magnitude, e.g., for the Al-vacancy from 0.2 to 2.3 kB.

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