Towards Accurate Predictions of Martensitic Transition Temperatures for Shape Memory Alloys from *Ab Initio* Simulations

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ABSTRACT

Experimentally, NiTi undergoes a single martensitic phase transition around 341 K from the low-temperature (T) monoclinic B19' phase ($P2_1/m$) to the high-temperature cubic B2 phase ($Pm\bar{3}m$). Theoretically, an orthorhombic B33 (*Cmcm*) has also been proposed as the T=0 ground state structure, although this phase has never been observed. Accurate predictions of martensitic transition temperatures (MTT) have remained elusive in part due to several well-known theoretical complexities of these systems including low temperature instabilities of the B2 phase. Recently, we proposed a rigorous thermodynamic integration approach based on *ab initio* simulations to resolve many of these difficulties [1,2]. However, an unsatisfying overprediction of the MTT relative to experiment (by ~100 K) means a fully quantitative theory is still lacking. In this work, we report several new developments to our method that bring first principles theory and experiment much closer into agreement. Our calculations indicate that phonon free energies at low temperature stabilizes B19' over B33, rationalizing B19' as the ground state down to T=0. We also find that accurate computations of the electronic free energy, i.e. the change in energy and the appearance of electronic configurational entropy due to finite temperature, is crucial to obtain accurate MTT. Incorporating these corrections results in an MTT prediction of 365 K for binary NiTi, which is in very close agreement with experiment. Our theoretical approach is expected to be a broadly applicable and predictive theory for MTT of SMAs.

[1] J.B. Haskins, A.E. Thompson and J.W. Lawson, Phys. Rev B 94, (2016) p. 214110
[2] J.B. Haskins, J.W. Lawson, J. App. Phys. 121, (2017) p. 205103