

Anharmonic Effects in Self-Diffusion Coefficients of Nickel

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Experiments reveal that self diffusion for many fcc and bcc metals is enhanced at high temperature, thereby deviating from expected Arrhenius behavior. This anomalous behavior remains poorly understood, even 50 years after its discovery. For nickel it is expected the deviation is caused by the influence of the di-divacancy mechanism in addition to the dominant single vacancy mechanism, but zero temperature *ab initio* calculations suggest this is not the case. We investigate finite temperature effects due to anharmonicities in the potential for the single vacancy mechanism in nickel using a classical EAM potential. We modify the recently developed Wang-Landau Monte Carlo method¹ to extract the vibrational density of states—or, equivalently, the free energy—along a continuous spatial reaction coordinate². This allows the calculation of transition rates within full transition state theory at finite temperatures, explicitly capturing all anharmonic terms of the potential which become more significant at high temperature. Our low temperature results agree with the harmonic approximation, and our high temperature results reveal a similar anomalous trend as seen in experiment! Hence, we propose a new solution to a long standing problem: anharmonicities of the potential near the single vacancy mechanism may be enough to explain the anomalous behavior of self-diffusion coefficients observed at high temperature in nickel.

[1] F. Wang and D. P. Landau, Phys. Rev. Lett. **86**, 2050 (2001).

[2] F. Calvo, Molec. Phys. **100**, 3421 (2002).