

## ***Effects of the vacancies and the external stress on the solubility and the diffusion of hydrogen in nickel from ab initio calculations***

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The incorporation of hydrogen in metals can strongly affect the physical properties of the host matrix and can lead to irreversible damages. Therefore, the solubility and the diffusion coefficient of hydrogen in metals are fundamental data to design new protections preventing hydrogen embrittlement and safety materials. However, the apparent solubility and diffusion coefficient can be influenced by the presence of crystalline defects such as point defects, dislocations or grain boundaries. In particular, it has been suggested that hydrogen promotes the formation of new vacancies, which participates to the mechanisms of degradation of metals<sup>1</sup>. In addition, the application of an external stress can deeply modify the solubility and the diffusion properties of H, which are implicated in the corrosion under stress processes. In this study, we use first principles calculations to determine the vacancy and hydrogen concentrations at thermodynamic equilibrium and the H diffusion coefficient up to the melting point.

First, we calculate the solubility and the vacancy concentration from the solution and H-vacancy complexes formation Gibbs free energies. We take into account an additional configuration part to the total entropy related to the distribution of H in the interstitial sites and the H-vacancy complexes. The calculations are performed up to the melting point for a wide range of H<sub>2</sub> chemical potential where the Gibbs free energy is expressed as a sum of vibration and electronic contributions from the computation of the phonon dispersion curve and the electronic density of states. We found that H-rich octahedral sites inside the vacancy core are destabilized at high H<sub>2</sub> chemical potential, similarly to fcc Fe<sup>2</sup>. A close agreement is found between experiments<sup>3</sup> and the hydrogen concentration calculated for a H<sub>2</sub> fugacity of 1 bar. In particular, we show that the electronic excitations lead to a positive deviation in the Arrhenius plot of the solubility at temperatures close to the melting point<sup>4</sup>.

The diffusion coefficient of H is calculated next. We use the transition state theory similarly to previous studies<sup>5</sup> and our results are consistent with experiments. In particular, we focus on the trapping/detrapping kinetic rates of H to move inside/outside of the vacancy. Finally, we discuss the effect of the application of an external stress on the H solubility and diffusion coefficient.

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