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Unified mechanism for hydrogen trapping at metal vacancies

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ABSTRACT

Interaction between hydrogen (H) and metals is central to many materials problems of scientific and technological importance. H segregation or trapping at lattice defects plays a crucial role in determining the properties of these materials. Through first-principles simulations, we propose a unified mechanism involving charge transfer associated strain destabilization to understand H segregation behavior at vacancies. We discover that H prefers to occupy interstitials with high pre-existing charge densities and the availability of such interstitials sets the limit on H trapping capacity at a vacancy. Once the maximum H capacity is reached, the dominant charge donors switch from the nearest-neighbor (NN) to the next-nearest-neighbor (NNN) metal atoms. Accompanying with this long-range charge transfer, the sharply increased reorganization energy would occur, leading to the instability of the H-vacancy complex. The physical picture unveiled here appears universal across the BCC series and is believed to be relevant to other metals/defects as well.

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Introduction

Interaction between H and lattice defects underlies diverse materials phenomena [1–4], including H storage [3,5], H embrittlement [6–8], metallic H membranes [9], nuclear fusion reactors [10,11] and H-assisted superabundant vacancy formation in metals [1,12,13], etc, to name a few. Crucial to all these problems is trapping of H at the lattice defects, such as vacancies, voids, dislocations, grain boundaries and cracks [14–22]. In particular, H trapping at vacancies has attracted great interest thanks to the facts that (1) vacancies are easier to study than other defects but have profound influences on

materials properties, (2) vacancies hold many surprises and mysteries yet to be explored, and (3) the insight gained from vacancies can be applied to other defects as well.

It have been theoretically found that, for BCC and FCC metals, at most six H atoms can be trapped by a monovacancy in general because H prefers to occupy the six octahedral (O) interstitials surrounding the vacancy [1,16,17]. However, there are exceptions that the maximum H capacity can go up to 10 for molybdenum (Mo) [16,17,23] and 12 for tungsten (W) [16] and aluminum (Al) [14]. In addition, various interpretations of the available experimental results have also been put forward: (i) The competition between metal-H hybridization and the Coulomb repulsion determines the position and number

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of H atoms around the vacancy in BCC-Fe [24], (ii) In comparison with Fe, the greater H trapping capacity in Al is attributed to a larger lattice constant and more delocalized electronic states [14], and (iii) for W, it was suggested that the vacancy provides an isosurface of optimal charge density that facilitates the formation of H bubbles [25]. Clearly, an important question to ask is whether or not there exists a unified mechanism of H trapping in metals?

In this paper, here we propose such a unified mechanism based on quantum-mechanical density functional theory (DFT) calculations. We have shown that the charge transfer associated strain destabilization is responsible for H trapping behavior around vacancies across the BCC series. By examining H trapping at monovacancies in these BCC metals (including V, Nb and Ta as good candidates for H storage, Mo and W as the most promising plasma facing materials of nuclear fusion reactors, and Fe and Cr as the most commonly used elements in H-resistant structural steels), we have discovered that H prefers to occupy the interstitial sites with

high pre-existing charge densities with or without a vacancy. The availability of such interstitial sites determines the H capacity around a vacancy. When the maximum H capacity is reached, the dominant charge donors switch from the NN to the NNN metal atoms. The long-range charge transfer associates with a significant strain energy cost. The correlation between the charge transfer and the onset of mechanical “instability” appears universal across the BCC series, and ultimately determines the limit on H trapping around a monovacancy in metals.

Theoretical methods

The DFT calculations have been performed by employing the Vienna ab initio Simulation Package (VASP) [26–28] with the projector augmented wave potential (PAW) method [29,30] and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [31] form was employed for

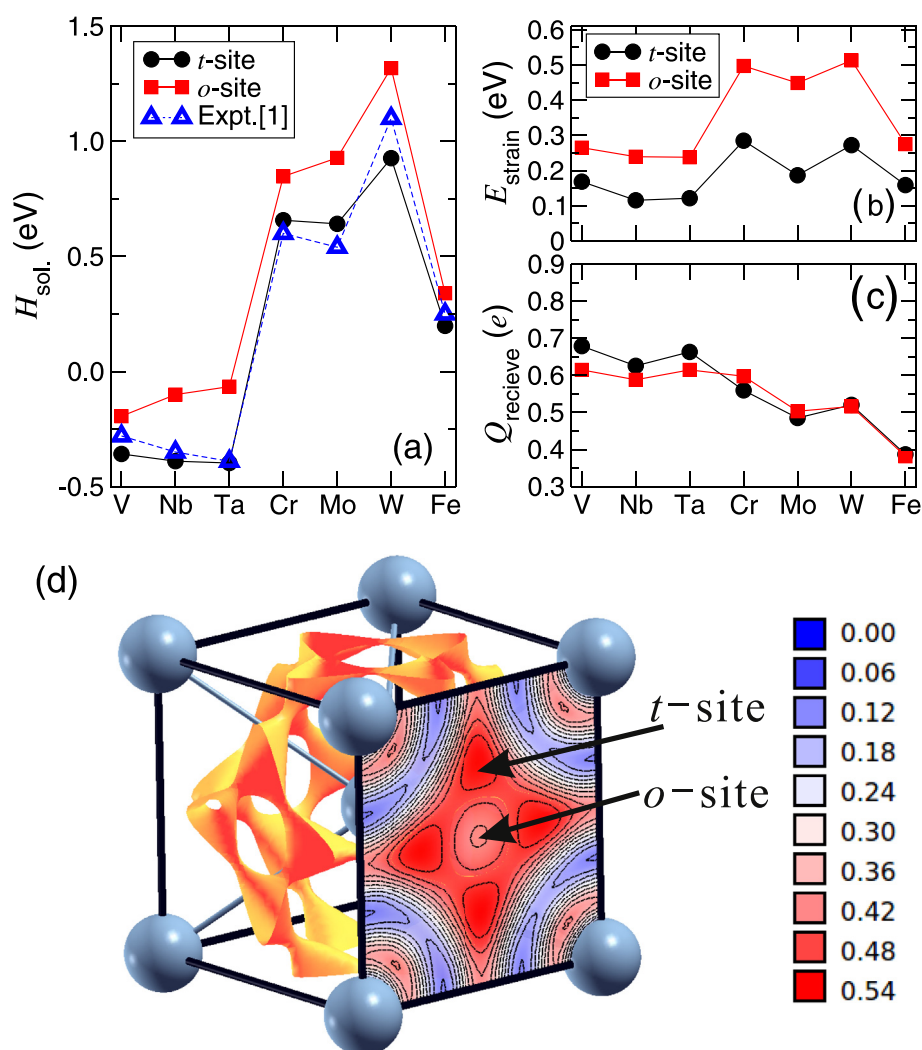


Fig. 1 – H in defect-free metals. (a) The solution enthalpies (along with available experimental data [1]) of H, (b) the strain energy induced by H insertion and (c) the received charges of H at T- or O-sites in seven BCC-type metals (V, Nb, Ta, Cr, Mo, W and Fe). (c) Isosurface (with an isovalue of 0.42) of the electron localization function (ELF) and its contour plot on (001) plane showing the highest charge densities at the T-sites in V. The similar results have been observed for other six BCC metals (Cr, Fe, Nb, Mo, Ta and W), but are not shown here.

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