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Ab initio modelling of Y and O solute atom interaction in small clusters within the *bcc* iron lattice

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Small yttrium and oxygen complexes in the *bcc* iron matrix are modelled by performing DFT calculations. The interaction between Y and O in isolated molecule, rock-salt crystal is compared with that in Y/O, Y/2O, 2Y/O clusters within the *bcc* iron matrix. Interaction energies and electron charge redistribution are also analysed. Among the clusters, the most stable ones are analysed further. It is shown that chemical bonding in YO molecule and crystal is significantly stronger than in the host matrix and the main interaction in the matrix occurs with nearby Fe atoms.

1. Introduction

Oxide Dispersed Strengthened (ODS) steels are considered to be promising materials for advanced fission and future fusion reactors due to their high radiation resistivity. ^[1, 2] The most common oxide for ODS steels is Y₂O₃, known for its high mechanical strength, temperature stability, chemical and erosion resistance. Introduced into the steel by mechanical alloying, followed by powder consolidation, yttria particles vary in size and shape. Atomic tomography experiments confirmed the presence of yttrium and oxygen within the host iron matrix also in a form of solute atoms. ^[3] It also has been demonstrated that ODS steels remain stable after being exposed to neutron radiation. ^[4, 5]

Interacting with each other, Y and O solutes give rise to various nanoclusters. Along with relatively large ODS particles, these small nanoclusters determine

stability of ODS steels. [6, 7, 8] *Ab initio* modelling of such clusters provides a deep insight into the interactions between impurities in ODS steels. [9, 10]

2. Method and model

Calculations were performed using the DFT method. [11] The computer code VASP 5.34 [12] is currently based on the PAW (Projected Augmented Waves) formalism [13]. Exchange-correlation functional is described by the PBE functional. [14] Plane wave basis set is limited by the cut-off energy value of 450 eV. Brillouin zone sampling [15] was realized in our simulations by the Monkhorst-Pack 4×4×4 scheme. [16] Total atomic structure optimisation was performed for all configurations, with the parameters of 4×4×4 supercell kept fixed. The electron charge transfer between V_{Fe} -stabilized Y and O solutes within the host Fe matrix was analysed by means of the Bader method. [17] The electron density redistribution was visualized, with respect to neutral isolated Y and O atoms, and the host matrix. Defect interaction energy was calculated with respect to single V_{Fe} , Y_{Fe} , O_{6b} or their combinations.

3. Results

For the reference, we calculated isolated YO molecule (**Figure 1 a**) and YO rock-salt structured crystal (**Figure 1 b**). Calculated binding energy for isolated molecule is -7.58 eV. Charged atoms (1.15 e) in YO molecule are found to be stabilized at the distance of 1.82 Å. In the rock-salt crystal Y-O bonds become longer – 2.41 Å due to the repulsion between large Y atoms. At the same time, charge polarization increases to 1.54 e . Binding energy, as expected, grows to -12.5 eV.

Earlier studies show that Y ion in *bcc* iron matrix requires vacancies for stabilization (**Figure 2 a**). With two vacancies Y ion is stable at 8c Wyckoff

position. ^[18] O ion, with a much smaller atomic radius, is stable at *6b* and *12d* sites ^[19] (**Figure 2 b**).

For the combination of Y at *8c* and two V_{Fe} with O at *6d*, all of the possible configurations in the $4 \times 4 \times 4$ supercell were investigated. The most stable configuration has the energy of -1.79 eV, which is significantly smaller than for isolated molecule. Occupying the nearest vacancy by oxygen atom is energetically unfavourable, so it remains at the interstitial *8c* site (**Figure 3a**).

The distance between Y and O in this configuration is slightly smaller than that in the rock-salt crystal – 2.35 Å. Y becomes positively charged by 1.25 e , while oxygen ion is charged by -1.31 e . Difference electron density map clearly shows that Y and O actively interact with the nearest Fe atoms (Figure 3c).

Further expansion of the system was performed by introducing one more oxygen solute to the most stable Y/O cluster. O atom was added at *6b* site at a distance of 1, 2, and 3 nearest neighbours (NN) from Y atom. All possible configurations at these distances were investigated and several stable configurations were found. The most stable one for OYO complex (Figure 4 a, b) possesses the Y/O –O binding energy of -1.39 eV. All solutes become charged stronger: Y – +1.35 e , O – -1.38 e . Analogously to the previous case, relatively weak charge transfer between Y and O ions has been observed (**Figure 4 c**).

In the energetically less favourable (-0.10eV) configuration for OYO combination (**Figure 4 d, e**), charge transfer between Y and O is more pronounced (**Figure 4 f**). Oxygen atoms in this configuration are charged by -1.27 e and -1.34 e . Y ion has practically the same charge as that in the most stable configuration for this set of defects - +1.37 e .

YO particles in iron matrix could also grow from yttrium clusters, accumulating oxygen. Without vacancies, two Y solutes are the most stable as 2NN substitutes (-0.12 eV). Several configurations for Y/O-Y system were tested, where Y atoms were placed at different distances at $2a$ sites of *bcc* elementary cell, with oxygen either in $2a$ or $6b$ site. Binding energies were calculated for all configurations.

The most stable configuration for -3Fe , 2Y_{Fe} and O with the binding energy of -4.21 eV is shown in **Figure 5 a, b**. In this configuration, both Y ions become charged by $1.20 e$, oxygen – by $-1.31 e$. Moving oxygen ion to $6d$ position between Y ions (**Figure 5 d, e**), decreases binding energy down to -3.39 eV and increases charge polarisation. Y ions become charged by $+1.25 e$ and O ion – by $-1.32 e$. In both cases, oxygen and yttrium atoms exchange the electron charge predominantly with the nearest atoms of the host matrix (**Figure 5 c, f**)

4. Analysis and conclusions

Interatomic distances between Y and O atoms in Fe matrix for stable clusters are close to those in YO crystal. Electron charge on both Y and O atoms increases in Fe matrix (compared to YO isolated molecule). The effect is catalysed by adding O solutes to the system and inhibited by adding Y solutes.

Chemical bonding between Y and O in yttria, YO molecule as well as YO rock salt crystal in comparison to that in *bcc* iron matrix is significantly stronger. Actively exchanging electron charge with the nearest iron atoms, oxygen and yttrium show practically no interaction. This effect can be seen on all difference electron density maps. The most illustrative is the system with two Y and O solute. In the larger distance configuration (**Figure 5 a**), Y atoms interacts with one particular Fe atom (**Figure 5 b**). When the distance between Y and O atoms is reduced (**Figure 5 d**), the same Fe atom is strongly polarized by oxygen (**Figure 5 e**) and at the same

time, Y atoms make other Fe atoms more polarized. Overall, at closer distances between Y and O binding energy become smaller.

At small concentrations of Y and O solutes, the main interaction occurs with the host matrix. Y and O may start interacting in the iron lattice only if their local concentration screens iron ions.

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