

## First-principles Study on the Properties of Point Defects in Hcp-Dy

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**Abstract.** This *Ab initio* density functional theory calculations have been used to study the properties of point defects for hexagonal close-packed (hcp) Dysprosium (Dy), e.g., the formation energies of self-interstitial atoms (SIAs), mon-vacancy, interstitial H atoms and interstitial He atoms. The results indicate that most of the self-interstitial configurations are stable. The formation energy of an interstitial H atom is less than that of a substitutional H atom, and it is also found that the formation energy of an interstitial He atom is smaller than that of a substitutional He atom in hcp Dy, which agrees with those results from other hcp structure metals.

### Introduction

Rare earths play an important role in advanced materials, they are used as catalysts in automotive catalytic converters, as iron and steel additives, as ceramic and glass additives, which attract much attention in computer simulation [1, 2]. One of the most interesting reasons is that rare-earth metals present a large affinity for hydrogen [2, 3]. Properties of self-interstitial atoms defects for some hcp structure metals have been calculated using *Ab initio* density functional theory calculations [4, 5]. Yang *et al* have studied the properties of H and He defects in hcp Sc and Er, and they found that, both H and He defects, the formation energy of an interstitial atom is less than that of a substitutional atom, Furthermore, the T (tetrahedral) interstitial position is more stable than an O (octahedral) position for both He and H interstitials in hcp structure Sc and Er [4, 5]. However, there are few studies on the properties of interstitial H atoms and He atoms in hcp Dy.

Interest in rare-earth hydrides has been stimulated in the last few years for several reasons [2-6]. As is well known, <sup>3</sup>He accumulates in the host metal as tritium decays via the reaction:  $T \rightarrow {}^3\text{He} + \beta^- + \bar{\nu}_e$  + 18.582 keV,  $\beta^-$  is a beta particle and  $\bar{\nu}_e$  is an antineutrino [7]. In the present work, the point defects properties of the self-interstitial atoms (SIAs), mon-vacancy, interstitial H atoms and He atoms in hcp-Dy have been investigated by *Ab initio* density functional theory, which are compared with the other hcp metals.

### Computational method

In our calculations, the point defects properties of hcp Dy were performed with the Vienna *Ab initio* Simulation Package (VASP) code [8]. These calculations involved the projector augmented wave (PAW) method [9], the exchange and correlation functions used in the present calculations were the generalized gradient approximation (GGA) of Perdew and Wang (PW91) [10], and the pseudopotential of Dy, H and He were taken from the VASP database, where the PAW potentials of H and He provide good descriptions for hexagonal close-packed structure Sc-H/Sc-He and

Er-H/Er-He systems [4, 5]. A  $4 \times 4 \times 4$  supercell (96 atoms) was employed to investigate the point defects, and gamma-centered grids were used in hcp-Dy. The atomic positions, supercell shape and supercell size were relaxed by using the plane-wave basis sets. In our calculations, the energy cutoffs of 300 eV for a perfect crystal, energy cutoffs of 400 eV for the H defects properties, and the energy cutoffs of 550 eV for He defects properties were performed. After the relaxations, the total energies of the calculated supercells were accurately determined.

The formation energy of SIAs in hcp-Dy can be defined by

$$E_i^f = E_{N+1}^{Dy} - (N + 1)\varepsilon_{Dy}, \quad (1)$$

in equations (1),  $E_{N+1}^{Dy}$  is the total energy of a supercell calculated in the present work, which contains a self-interstitial Dy atom,  $N$  is the number of atoms in the perfect hcp computational cell,  $\varepsilon_{Dy}$  denotes the energy of a Dy atom in a perfect hcp-Dy crystal [5].

The formation energies of a H atom, He atom and vacancy in hcp-Dy can be calculated by

$$E_{A_n V_m}^f = E_{A_n V_m}^{total} - (N - m)\varepsilon_{Dy} - n\varepsilon_A, \quad (2)$$

in equations (2), A denotes He or H atom, when  $n=0$  and  $m=1$ ,  $E_{A_n V_m}^f$  is the mon-vacancy formation energy, when  $n=1$  and  $m=0$ ,  $E_{A_n V_m}^f$  represents the formation energy of an interstitial He or H atom, and when  $n=1$  and  $m=1$ ,  $E_{A_n V_m}^f$  denotes the formation energy of a substitutional He or H atom.  $E_{A_n V_m}^{total}$  is the total energy of the calculated supercell containing a defect,  $N$  is the number of Dy atoms in the perfect hcp computational cell,  $\varepsilon_{Dy}$  and  $\varepsilon_A$  respectively denote the energy per Dy atom in a perfect hcp-Dy crystal and the energy a He atom or H atom [4].

The notations of self-interstitial atom configurations and defect complex  $E_{A_n V_m}^f$  configurations in hcp-Dy can reference Ref. 11 and 12. As shown in Fig. 1, T denotes tetrahedral interstitial configuration, O represents octahedral configuration, C stand for crowdion, S is split dumbbell, and BT, BO, BC, and BS are the corresponding basal plane positions [11, 12].

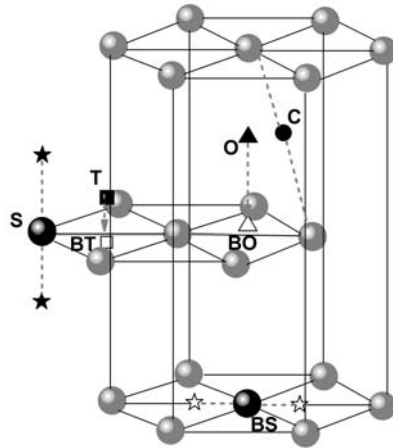


Fig. 1. The several interstitial configurations in hcp-Dy.

## Results and discussion

Using density functional theory calculations with the chosen pseudopotentials, the calculated equilibrium lattice parameters for hcp-Dy were 3.595 Å and 5.648 Å, both are in good agreement with the experimental values ( $a = 3.592$  Å,  $c = 5.655$ ) [13]. In our calculations, the convergence of the formation energies of SIAs with respect to the k-points is tested as shown in Table 1. It is found from Table 1 that the calculated formation energies for the SIAs of several possible configurations more or less depend on the k-points, but these formation energies converge at the  $4 \times 4 \times 4$  k-points. Thus, the  $4 \times 4 \times 4$  k-points are used for the followed calculations of interstitial H and He atoms.

Table 1. Formation energies (in eV) for the SIAs of several possible configurations in hcp-Dy

Supercell size	Energy cutoff	k-points	O	S	C	T	BO	BS	BT	V
4×4×4 (96 atoms)	300 eV	6×6×6	2.44	2.76	2.73	2.82	2.13	2.55	3.10	
		4×4×4	2.44	2.78	2.74	2.83	2.14	2.54	3.19	1.72
		2×2×2	2.46	2.82	2.75	2.86	2.15	2.58	3.26	

It is also can be found that the three calculations with different k-points show the same relative stability of the several self-interstitial atom configurations, e. g., the most stable configuration of the seven SIAs is BO, followed by O, BS, C, S, T, the BT configuration has the largest formation energy, which is similar to the relative stability of SIAs in hcp-Er [5] and hcp-Y [12].

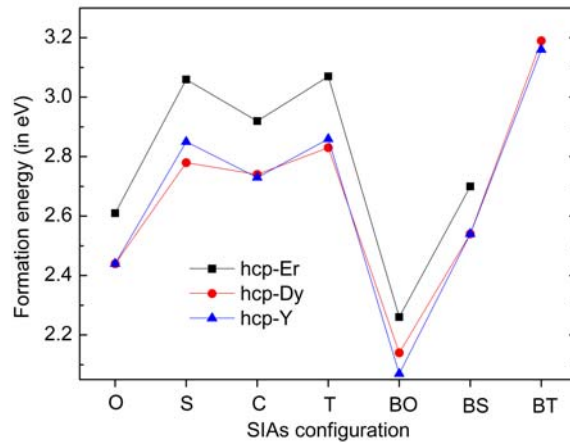


Fig. 2. The several formation energies of SIAs in hcp-Dy, hcp-Er, hcp-Y.

As shown in Fig. 2, it is clearly found that there is a similar tendency of the relative stability of SIAs in hcp structure Dy, Er, Y, which may be due to the same hcp lattice sites.

The formation energies of interstitial atoms (H, He) and substitutional atoms (H, He) in hcp-Dy have been determined as shown in Table 2. The formation energies of substitutional atoms (H, He) are denoted with “Sub”. In the present calculations, the 4×4×4 supercell was used.

Table 2. Formation energies (in eV) for the H and He point defects of several possible configurations in hcp-Dy.

Interstitial atom	k-points	Energy cutoff	O	S	C	T	BO	BS	BT	Sub
H	4×4×4	500 eV	-0.75	-0.95	0.01	-0.96	-0.15	-0.85	-0.85	2.40
He		550 eV	1.92	1.90	1.94	1.69	1.76	2.05	1.71	2.54

The calculated results show that the formation energy of T configuration for H is the least one, followed by S, BS, BT, O, BO, C and Sub configurations, which indicates that T configuration of H is the most stable interstitial configuration in hcp-Dy. The present calculations show that the relative stability of T, BT, O and BO configuration for H is similar to that in hcp-Er and hcp-Y [5, 12]. The formation energy of a substitutional H atom is 2.40 eV, even taking into account the formation energy of mon-vacancy (1.72 eV), the value of the formation energy of a substitutional H atom is also the biggest one, which means that the H atoms prefer to occupy interstitial sites in hcp-Dy.

As shown in Table 2, we have also investigated the formation energies of He atoms for several possible configurations in hcp-Dy. Considering the formation energy of mon-vacancy (1.72 eV), the formation energy of a substitutional He atom with the value of 0.82 eV is the least one, which suggests that the He atom in hcp-Dy prefers to the vacancies.

## Summary

The formation energies of self-interstitial atoms (SIAs), interstitial H atoms and interstitial He atoms in hcp-Dy have been investigated by first-principles method based on density functional theory. The present results demonstrate that the most stable configuration of the seven SIAs is BO configuration, followed by O, BS, C, S, T and BT configurations in hcp-Dy. The calculations on interstitial H atoms show that the formation energy of T configuration for H is the least one, followed by S, BS, BT, O, BO, C and Sub configurations. The formation energy of a substitutional H atom is larger than that of calculated interstitial H configurations, which suggests that the H atoms prefer to occupy interstitial sites in hcp-Dy. While the formation energy of a substitutional He atom adjusted to the formation energy of mon-vacancy (1.72 eV) is less than that of interstitial He atoms, which suggests that the He atom in hcp-Dy prefer to the vacancies.

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## References

- [1] W.Y. Hu, H.Q. Deng, X.Y. Yuan and M. Fukumoto: The European Physical Journal B-Condensed Matter and Complex Systems Vol. 34 (2003), p. 429
- [2] C.M. Parish, C.S. Snow and L.N. Brewer: Journal of Materials Research Vol. 24 (2009), p. 1868
- [3] T. Palasyuk, M. Tkacz and P. Vajda: Solid State Communications Vol. 135 (2005), p. 226
- [4] L. Yang, S.M. Peng, X.G. Long, F. Gao, H.L. Heinisch, R.J. Kurtz and X.T. Zu: Journal of Physics: Condensed Matter Vol. 23 (2011), p. 035701
- [5] L. Yang, S.M. Peng, X.G. Long, F. Gao, H.L. Heinisch, R.J. Kurtz and X.T. Zu: Journal of Applied Physics Vol. 107 (2010), p. 054903
- [6] K.M. Fan, L.Yang, Z.Y. Zhang, S.M. Peng, X.G. Long, X.S. Zhou, X.T. Zu and F. Gao: The European Physical Journal B Vol. 87 (2014), p. 295
- [7] D.J. Mitchell and J.L. Provo: Journal of Applied Physics Vol. 57 (1985), p. 1855
- [8] G. Kresse and J. Hafner: Physical Review B Vol. 47 (1993), p. 558
- [9] G. Kresse and D. Joubert: Physical Review B Vol. 59 (1999), p. 1758
- [10] J.P. Perdew, J.A. Chevary, S.H. Vosko and C. Fiolhais: Physical Review B Vol. 46 (1992), p. 6671
- [11] R. A. Johnson, J. R. Beeler: *Interatomic Potentials and Crystalline Defects* (AIME, New York 1981).
- [12] K.M. Fan, L.Yang, J. Tang, Q.Q. Sun, Y.Y. Dai, S.M. Peng, X.S. Zhou and X.T. Zu: Chinese Journal of Chemical Physics Vol. 26 (2013), p. 526
- [13] R. A. Johnson, J. R. Beeler: *Structure of Metals* (Pergamon Press, Oxford 1980).