Light impurity atoms as the probes for the electronic structures of actinide dioxides

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ABSTRACT

First-principles density functional theory are used to calculate the formation energies of ten light impurities X (X: H, He, Li, Be, B, C, N, O, F and Ne) in seven actinide dioxides AnO_2 (An: Th, Pa, U, Np, Pu, Am and Cm), in order to elucidate the relative stability of X and to obtain some trends of impurities behaviors. The Hubbard parameter U is used to describe the strongly correlated electron behavior of An 5f electrons. The results indicate that the formation energies of X significantly depend on the properties of AnO_2 and X. For X at the octahedral interstitial sites of AnO_2, F is the only energetically favorable impurity for all AnO_2, owing to its strong oxidability; H in PaO_2, O in PaO_2 and UO_2, Li in PuO_2, AmO_2 and CmO_2, Be in AmO_2 and CmO_2 are also energetically favorable. The oxidability or reductivity of X and the delocalization → localization transition of 5f electrons across actinide series can account for the trends of the behaviors of X in AnO_2. Particularly, H, a very typical amphoteric element, is chosen to illustrate its difference existence states in AnO_2. H prefers to occupy the octahedral interstitial sites of early AnO_2 or form hydroxyl group in the later AnO_2.

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1. Introduction

Nowadays, the materials with fascinating properties and potential applications have attracted the extensive research interests. Even so, the actinide materials remain the challenging field from the point of view of fundamental science because they contain a plethora of interesting physical and chemical behaviors. Essentially, how to understand the complicated and environment-sensitive 5f electronic states of actinide materials is of central importance in the field [1]. Many experimental and theoretical efforts have been devoted to probe the intrinsic behaviors and trends of 5f electrons across the actinide series. Two series of typical actinide materials, i.e., metals (or alloys) and oxides, are widely studied. A paramount standpoint is that 5f electrons occur the delocalization → localization transition across actinide series and Pu just lies at the critical position of the transition. Correspondingly, Pu-based materials are mostly concerned among all the actinide materials [2,3]. With the development of advanced experimental and theoretical techniques, the electronic structures of Pu materials have been understood, at least partially. Particularly, the discoveries of the first Pu-based superconductors $PuCoGa_5$ and the subsequent actinide-based superconductors

greatly facilitate the comprehensive understanding of the 5f electronic states. For example, the fluctuations among Pu 5f electronic configurations of many Pu materials are determined to be in the range of $5f^4$–$5f^6$, and the concrete values of 5f occupations or the occupation ratio of 5f/6d, are very sensitive to the chemical and physical surroundings [4–6].

Available experimental and theoretical data on the electronic structures of actinide materials mainly concentrated on their perfect crystal structures. However, impurities are ubiquitous in the processes of production, purification, fabrication, storage and application of actinide materials. Moreover, owing to their radioactivity and fissionability, many radioactive and fission products continuously accumulate in the hosts [7]. Knowledge from impurities in solid state materials, an old but engaging scientific topic, shows that impurities may play a decisive role in the properties of the hosts [8]. An outstanding example is the research and development of conventional semiconductors, in which impurity atoms even at very small concentration significantly influences the electronic properties. The properties of semiconductors could benefit from impurities doping. On the contrary, the impurity effects in actinide materials are generally negative. A very typical instance is that the rare gases (RG) transmuted in actinide materials could cause gas bubble formation, swelling, microstructure alteration and property degradation. In fact, available data regarding impurities in actinide materials mainly focused on the understanding of RG behaviors

[9–15]. Yet, the trends and the comprehensive understanding of RG behaviors are still unobtainable. This is mainly due to the difficulties in both experimental and theoretical handing of those radioactive and strongly-correlated electron materials. Apart from RG, the behaviors of other impurities have been fragmentarily reported [16–19].

In the present work, under the frameworks of density functional theory (DFT), we focus on the ten light impurities X (X: H, He, Li, Be, B, C, N, O, F and Ne) in the seven early actinide dioxides AnO_2 (An: Th, Pa, U, Np, Pu, Am and Cm) to find some trends of impurity effects and the perturbation of impurities on the electronic structures. Other impurities with larger atomic size are temporarily not considered mainly due to the well-known fact that the size effects of impurities are remarkable. Therefore, large supercell models are required to eliminate unreasonable expansion or lattice distortion. Consequently, the calculation consumption is so expensive that it is unpractical to capture the trends of impurity effects. As mentioned above, actinide metals (or alloys) and oxides are mostly concerned among all the actinide materials. For the former series, the electronic and crystal structures are significantly different; as a result, the series are not so straightforward for the study of impurity effects. In order to obtain the delicate differences in the impurity effects among actinide materials, actinide dioxides are proposed to be the ideal series because they crystallize in the same face-centered cubic (fcc) fluorite structure and exhibit the similar semiconducting behaviors [20–22]. Moreover, the impurity effects in actinide dioxides are the pressing topic in the context of nuclear fuel cycles and surface science. Note that, for the first actinide element Ac, "AcO_2" does not exist because the ground state configuration of Ac is $6d^1 7s^2$; therefore it's predominant oxidation state is +3, i.e., in the form of Ac_2O_3. On the other hand, the understanding of heavier actinides is rudimentary, with the level of comprehension decreasing with atomic number [23]. For this reason, the heavier actinide dioxides beyond CmO_2 are not considered.

2. Computational details

Total energy and electronic structure calculations are performed using the VASP code with PAW pseudo-potentials and PBE + U functional in the Dudarev formalism [24,25]. A universal Hubbard parameter U ($U_{eff} = U - J$) of 4 eV is selected for all the actinide 5f electrons. It is worth pointing out that other U values slightly deviated from 4 eV are demonstrated to be insignificant for the formation energy of impurities. For their magnetic orders of AnO_2, we use the widely accepted collinear $1 - k$ antiferromagnetic (AFM) states along the (1 0 0) direction. Our calculations and some similar calculations by other researchers show that the AFM states are generally energetically more favorable than nonmagnetic (NM) and ferromagnetic (FM) states [20,21,26,27]. Complete relaxation is employed for AnO_2 with or without impurities. Convergence is reached when the total energies converge within 1×10^{-5} eV and the Hellmann-Feynman forces on each ion are less than 0.02 eV/Å. The use of a plane-wave kinetic energy cutoff of 500 eV and $9 \times 9 \times 9$ Monkhorst-Pack k point sampling are shown to give accurate energy convergence. For the density of state (DOS) calculations, the tetrahedron method with Blöchl correction is used for the Brillouin-zone integration.

In fact, we make some tests (pseudopotentials, U values, energy cutoff, k points, etc.) mainly on UO_2 and PuO_2 with the octahedral interstitial site (OIS) O to ensure the validity of calculation methods [26,27]. We find that the variation arising from using different potentials and different U values for the formation energy lies in the range of ±0.1 eV. The magnetic orders such as the collinear and noncollinear AFM configurations have insignificant influence on the formation energy as well. For the sake of computational effi-

ciency, we decide to leave more complicated non-collinear AFM configurations outside of scope for our present calculations. Moreover, spin-orbit coupling (SOC) interactions have also been proven by our calculations and other researchers' calculations to be negligible for the formation energy despite that SOC may play an important role in predicting ground state of actinide materials. This is mainly due to the fact that the possible calculated energy errors in AnO_2 with and without impurity atoms using the same theoretical methods are approximately identical.

Pure spin-polarized DFT calculations are performed to determine the total energies of impurities. We use half the total energy of a diatomic molecule (e.g., H_2, O_2, N_2 and F_2) as the total energy of an impurity atom. Because of the well-known disadvantages of pure DFT in describing molecules, the scheme selected to calculate the total energy of a diatomic molecule is similar to the one proposed by Korzhavyi et al. [28]. For example, the total energy of H_2 is obtained by the sum of the energy of free atom H and the well-established dimerization energy (i.e., the reaction energy of $2H = H_2$). The total energy of a free atom is calculated by using a periodic cubic cell with a lattice constant of 15 Å and only one k point Γ. The total energies of RG atoms are calculated by this method. Both B and C are in the states of molecular crystals under standard conditions; therefore, we calculate the total energy of their molecular crystals (i.e., α-B and graphite) to obtain the total energy of single B and C atoms. Similarly, we calculate the total energy of Li and Be crystals (i.e., bcc and hcp structures) to obtain the total energy of single Li and Be atoms.

We first derive and examine the influence effects of impurities at the OIS of AnO_2 as shown in Fig. 1(a), paying close attention to impurity H, a very typical amphoteric element [29–31]. The formation energy of H along the pathway from its nearest neighboring O to the OIS (containing 21 sites for each dioxide) are considered, as indicated by the red arrow in Fig. 1(b). Afterwards, we conduct the calculations on the impurities in An and O vacancies of AnO_2, respectively.

3. Results and discussion

From the theoretical calculation point of view, defect formation energy (E_f) is the foremost quantity for the description of defective systems. E_f of defect X in charge state q is normally defined as

$$E_f[X^q] = E_{tot}[X^q] - E_{tot}[bulk] - \sum_i n_i \mu_i + qE_F + E_{corr}, \tag{1}$$

where $E_{tot}[X^q]$, $E_{tot}[bulk]$, μ, E_F and E_{corr} denote total energy of the perfect cell, total energy of the defective cell, chemical potential of the species added to or removed from the cell, Fermi energy and correction term accounting for electrostatic interactions, respectively [8,32]. Here, the energy of single atom (gaseous states for H_2, He, N_2, O_2, F and Ne; solid states for Li, Be, B and C) is selected for μ_i, which is a widely accepted treatment. Principally, we can compare the stability of impurity with different charge q; however, the trends on the behaviors of charged impurities in actinide dioxides are not so clear from our calculation results on charged (negative or positive) H. In the current calculations, we focus on the behaviors of impurities with neutral charge for the discussion of their perturbation on actinide dioxides. Moreover, for the incorporation sites of impurities, the trends derived from OIS are generally quite straightforward [33] and discussed in detail.

In Fig. 2, we present the calculated $E_f[X]$ of the ten impurities at the OIS of AnO_2. At first view, one can find the remarkable differences in the quantities of $E_f[X]$, no matter $E_f[X]$ represent an impurity element in different AnO_2, or an AnO_2 incorporated by different impurity elements. Despite the difficulty in describing the quantitative trends in Fig. 2, some interesting trends emerge from the qualitative analysis in terms of the properties of AnO_2