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Theoretical study on the alloying behavior of γ-uranium metal: γ-uranium alloy with 3d transition metals

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Abstract

We have investigated the alloying behavior of γ-uranium with 3d transition metals (TMs) using the relativistic discrete-variational Dirac–Fock–Slater (DV-DFS) method. The d-orbital energy (Md) as an alloying parameter well reproduces the alloying behavior of γ-uranium metal with TMs: (1) in the case of a large Md value (Ti, V, Cr), the solubility of these TM elements in γ-uranium becomes large; (2) in the case of a middle Md value (Mn, Fe, Co), the tendency to form a uranium intermetallic compound with these elements becomes stronger; (3) in the case of a small Md value (Cu), the alloying element is insoluble in γ-uranium. The alloying behavior of γ-uranium with TMs is also discussed in terms of other parameters such as electronegativity and metallic radius.

PACS: 70.20; 71.15.M; 71.20.B

1. Introduction

Metallic uranium has three phases, α (orthorhombic), β (tetragonal) and γ (body centered cubic: bcc). Both α- and γ-phase uranium (U) alloys are extensively studied for practical use in the field of nuclear science and technology. The uranium alloys has three kinds of structural types, solid solution, intermetallic compounds, and no alloys with other elements.

Titanium (Ti) dissolves mutually in γ-U and other six elements from vanadium (V) to nickel (Ni) partially dissolve in γ-U. Only copper (Cu) is insoluble with γ-U. Uranium alloys have been studied thermodynamically by Weigel [1] and Vambersky et al. [2]. However, the mechanism on the solubility of 3d TMs into the γ-U is still unclear. The aim of the present study is to understand the alloying behavior of γ-U by first-principle calculations of the electronic structure of γ-U-3d TM alloys.

The dissolution of 3d TMs in γ-U can be characterized by the electronic structure of the alloys. Morinaga et al. [3,4] applied the DV-Xα method to understand the alloying behavior of 3d, 4d and 5d TMs in super Ni_3Al, titanium, iron, and aluminum alloys, and succeeded in designing new high-temperature alloys by introducing two parameters: 3d orbital energy (Md) and the bond overlap population (Bo). Md is related to the charge transfer between base metal and 3d alloying element, while Bo is a good indicator for the strength of covalent bonding in the alloy. In a similar manner, we focused on

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Md of alloying 3d TMs to reveal the alloying behavior of γ-U alloy with 3d TMs.

2. Computational method

The DV-DFS molecular orbital (MO) is based on the Dirac–Fock–Slater (DFS) approximation [5–7]. This method provides a powerful tool for the study of the electronic structures of molecules containing heavy elements such as uranium [8–11]. The one-electron molecular Hamiltonian, **H** in the DFS MO method is written as

$$\mathbf{H} = c\alpha\mathbf{P} + \beta mc^2 + V(r), \tag{1}$$

where c, $\mathbf{P}$, m, α, β and $V(r)$ denote the velocity of light, the operator of momentum, the rest mass of electron, Dirac matrices and the sum of Coulomb and exchange potential, respectively. The molecular wavefunctions were obtained by taking linear combinations of atomic orbitals. The details of the DV-DFS method and the computational code used in the present work have been described elsewhere [5,12].

The basis functions, which were numerical solutions of the atomic DFS equations for an atomic-like potential, were obtained at the initial stage of each iteration of the self-consistent procedures [13]. The atomic-like potentials for generating the basis functions were derived from the spherical average of the molecular charge density around nuclei. One-center (atomic) charges were estimated in terms of the Mulliken populations [14] by the self-consistent charge (SCC) method [15], which was used to approximate the self-consistent field. All the DV-DFS calculations were performed with the Slater exchange parameter α of 0.7 and with 18,000 DV sample points. The basis functions for uranium atoms were up to 7p orbital, while that for 3d transition metal atoms up to 4p. The calculations were carried out self-consistently until the difference in orbital populations between the initial and final stages of the iteration was less than 0.01.

Fig. 1 shows schematic representation of a cluster model for γ-U-3d TMs alloys. As shown in Fig. 1, centered uranium atom can be substituted for alloying 3d TMs. This cluster model is an enough size to investigate fundamental features of the electronic structure of 3d TMs in γ-U [3,4]. We did not consider the lattice relaxation caused by element substitution in the present calculations. The lattice constant of γ-U crystal used in the calculation is 6.659 a.u. [16].

In order to analyze the electronic structure of γ-U-3d TM alloy, we obtained density of states (DOS), energy level structures, and orbital populations. The 3d ($3d_{3/2}$, $3d_{5/2}$) orbital energy for the alloying elements and the 6d ($6d_{3/2}$, $6d_{5/2}$) and 5f ($5f_{5/2}$, $5f_{7/2}$) orbital energies for uranium were evaluated from a weighted average of each component. The 3d and 6d orbital energies for alloying atom and γ-U were obtained by using Morinaga's method [3], respectively. The 3d orbital energy for TMs was expressed as Md, while that for centered uranium U(1) as Ud in the present work. The 5f orbital energy for U(1) and U(2) of γ-U was also expressed as Uf. Fig. 2 shows schematic outline of the alloying parameter. Uranium forms alloy with 3d TMs by the charge transfer. If the d and f orbital energy levels in γ-U are higher than Md, the charge transfer from TM to U occurs after bonding as shown in Fig. 2. The relative energy level is related to electronegativity [17] of the alloying elements. To investigate the change in the electronic structure by replacing the center 3d alloying atom, we analyzed the DOS both of the 5f and 6d orbitals for matrix γ-U and of the 3d orbital for the alloying elements.

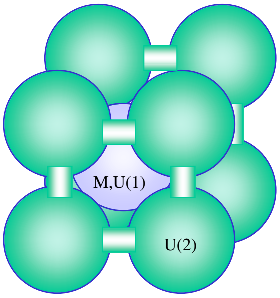

Fig. 1. Model cluster of γ-U alloys with 3d transition metal.

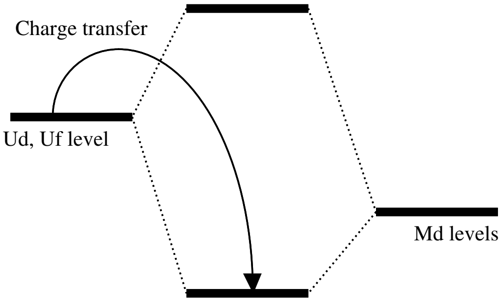

Fig. 2. Parameters used for alloy design, the d, f, orbital energy levels (Md, Ud and Uf).

3. Results and discussion

3.1. Energy level structure and d-orbital energy, Md

Fig. 3 shows the partial DOS of the 5f and 6d orbital components of U(1) and of the 3d orbital of the alloying elements in γ-U alloy. The Fermi level, Ef, was taken to be zero in the MO energy. The partial DOS of the $5f_{5/2}$, $5f_{7/2}$ and $6d_{3/2}$, $6d_{5/2}$ orbitals for pristine γ-U was indi-

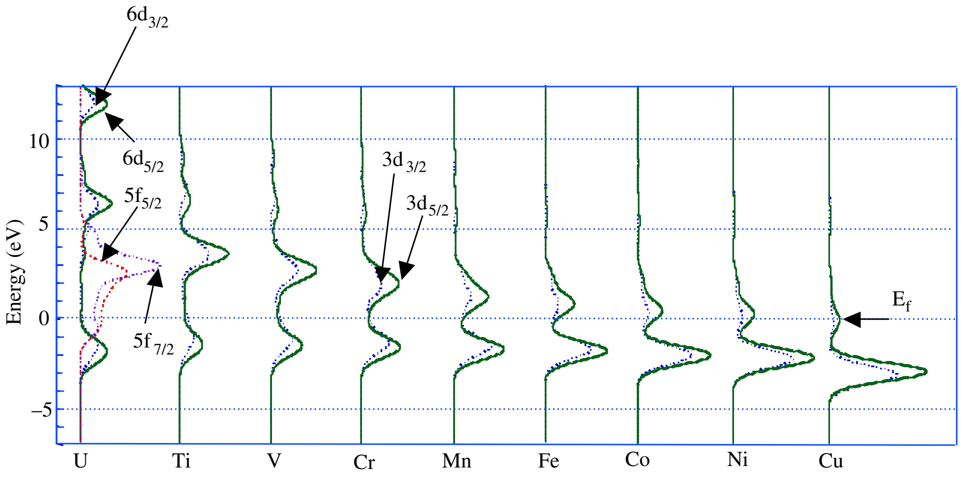

Fig. 3. Partial density of states for *d*-electrons of alloying elements in γ-U.

cated as a reference. The distribution of $3d_{3/2}$ and $3d_{5/2}$ near the Fermi level was shown in Fig. 3 for Ti to Cu element. As we examined partial DOS of the 5f and 6d orbital component for γ-U, U 5f was a major component and 6d component was negligible at the Fermi level. The peak of U6d component was located by a few eV below the Fermi level, the $U5f_{7/2}$ component in the energy region appears as slightly mixing with $U6d_{3/2}$ and $U6d_{5/2}$ component. It was found that the 3d orbital energy decreases with increasing the atomic number. The number of *d*-electron increases from 2.73 (Ti) to 9.40 (Cu) with the atomic number. This is because

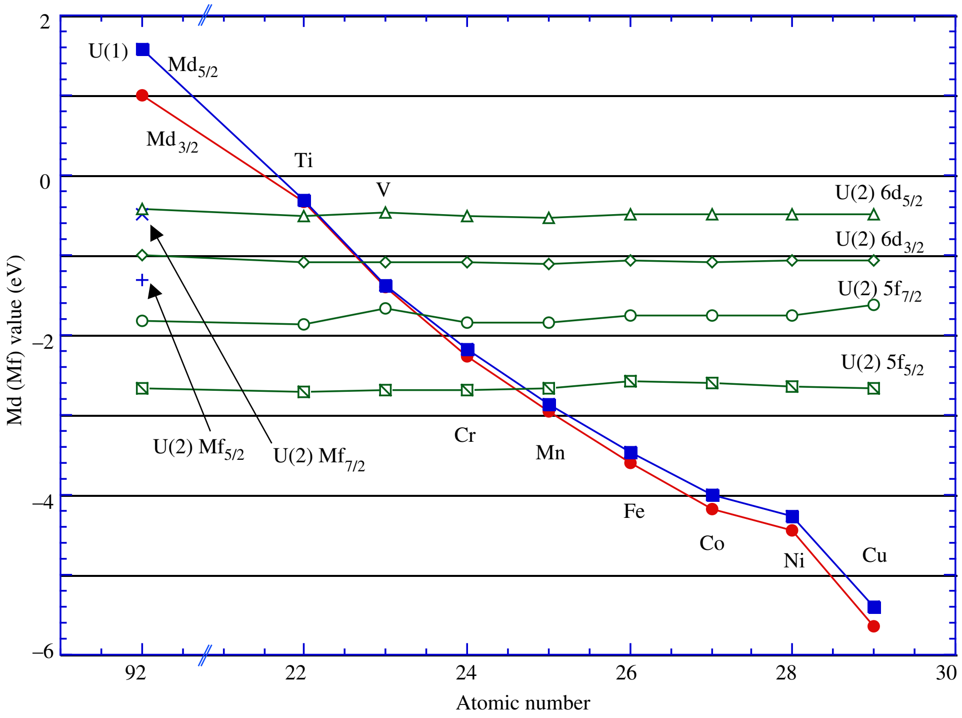

Fig. 4. Changes in the d, f-orbital energy, Md and Mf, respectively in γ-U-3d transition metal alloy. U(1): center atom before alloying, U(2): neighbor atom for alloying atom.

incompleteness of the degree of shielding effect for *d*-electron more than *s*-electron [3,4]. As shown in Fig. 3, the area of 3d partial DOS in occupied energy region increases with the atomic number.

Fig. 4 shows the change of Md values for the alloying element and of Ud and Uf values for U(2) as a function of the atomic number. The Ud and Uf energies for U(1) before alloying were indicated in Fig. 4. The Md decreases monotonously with increasing the atomic number. On the other hand, U(2)d$_{3/2}$, U(2)d$_{5/2}$, U(2)f$_{5/2}$, and U(2)f$_{7/2}$ were almost constant. Relative position of the Md value has clear relation to the charge transfer as shown in Fig. 2. To discuss the trends of Md value with respect to the alloying behavior, we compared these Md values with electronegativity and metallic radius.

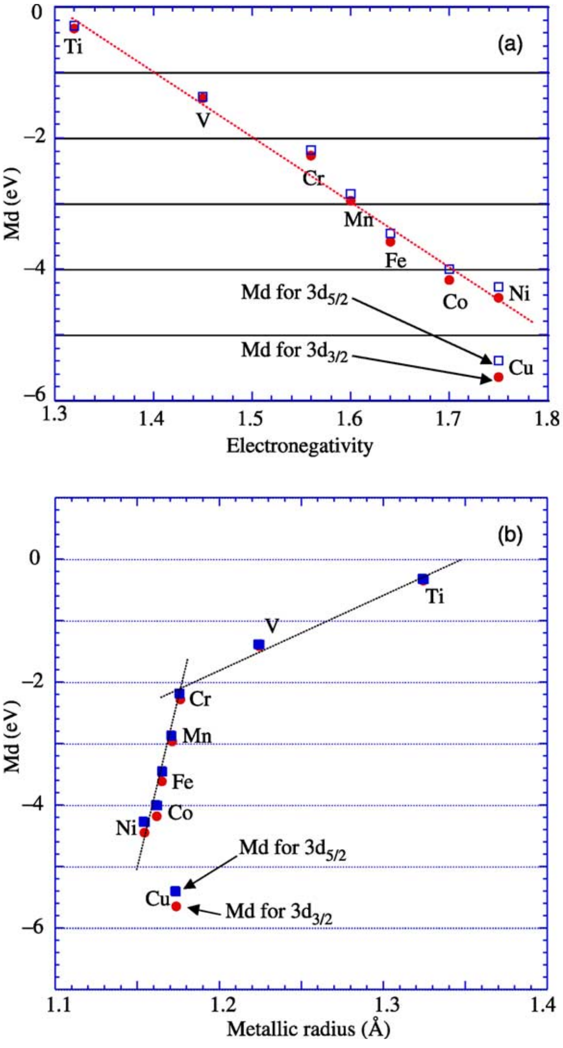

Fig. 5. (a) The correlation between the Md and the electronegativity. (b) The correlation between the Md and the metallic radius.

Fig. 5(a) shows the correlation between Md and electronegativity [17]. The Md value decreases with increasing the electronegativity of 3d TMs. The Md has a good correlation with the electronegativity and this behavior has been studied for nickel based superalloy so far [3]. As the electronegativity of alloying atom becomes lower, the atom tends to provide more electrons to the surrounding atom. We obtained a good correlation between the electronegativity and Md. Copper(Cu) takes a lower Md value compared with Ni and was only exception of linear relationship between the electronegativity and Md.

Fig. 5(b) shows the correlation between Md and metallic radius [18,19] of 3d TMs. The Md becomes larger with increasing the metallic radius. There is a bend in the line at Cr, as shown in Fig. 5(b). Namely, the Md decreases gradually with the metallic radius from Ti to Cr and decreases sharply from Cr to Ni. The Cu is also the exception of the Md versus metallic radius relation map. From this figure, the Md–metallic radius relationship was classified into three regions: (1) high Md with larger metallic radius (Ti, V and Cr), (2) lower Md with smaller metallic radius (Mn, Fe, Co and Ni), and (3) the lowest Md with smaller metallic radius (Cu). These three regions correlates to the solubility and stability of 3d TMs in the γ-U. As the metallic radius is larger, the mean radius of d-orbital becomes larger. As a result, the restrained force of *d*-electron given by centered nuclei becomes lower. The atom with a larger electronegativity and a smaller metallic radius has a higher Md. However, the behavior of Cu is different from that of other elements, which may be related to fully occupied d-orbital of Cu.

3.2. Stabilities of the γ-U alloy with 3d transition metal

The feature of γ-U alloy with 3d TMs is divided into 3 types as follows [20,21]: (1) wide range mutual solid solubility (Ti), (2) small amount of solid solubility, i.e. ca. 10 at.% solid solubility in γ-phase uranium (V) and less than 5 at.% solid solubility in γ-U (Cr, Mn, Fe, Ni, Co), and (3) insoluble with each other (Cu). As briefly described in the Fig. 2, the Md value is quite informative for the qualitative estimation of alloying behavior. Comparison among Fig. 4, Fig. 5(a) and (b) indicates that the tendency of solid solubility for 3d TMs in γ-U is confirmed with relation between Md and metallic radius. This can be explained from Md of alloying parameter and metallic radius of classical alloying parameter due to Hume-Rothery [22]. The copper takes the lowest Md value and solid solubility in this system. For alloying elements with atomic number from $Z = 24$ to 28 (Cr to Ni), Md further increases from Cr to Ti, while mutual solid solubility in γ-U with Ti decreases from 10 at.% (V) to below 5 at.% (Cr).

4. Summary

We have carried out the DV-DFS calculations on the γ-U alloys with 3d transition metal. The 3d orbital energy, Md, is a good index on the prediction of alloying behavior and solid solubilities of 3d TMs into γ-U. The relation between Md and metallic radius is indicative of the tendency of solid solubility for 3d TMs in γ-U.

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