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Relativistic density-functional study of the solid solubility of transition metal/γ-uranium alloys: The role of d–d orbital interactions

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ABSTRACT

The alloying behavior of transition metals (TMs) in solid γ-phase uranium (γ-U), which is expected to be used as fuel for next-generation nuclear reactors, was investigated using the discrete–variational Dirac–Fock–Slater molecular orbital method. Using a model cluster, U_8/TM, as the minimum unit of γ-U/TM alloys, we evaluated the d-orbital energy of the TM (Md), the bond order between the TM and U atoms, and the orbital overlap population (OOP) between the atomic orbitals of the TM and U atoms. We subsequently examined the effect of these quantities on the maximum solid solubility (MSS) of the γ-U/TM alloys. The interaction between the U-6d and TM-d atomic orbitals was found to play a key role in determining the MSS of the γ-U/TM alloys. The magnitude of the MSS can be explained in terms of the stabilization energy, which is affected by the Md and the OOP, formed by d–d orbital interactions. We also mapped the MSS of γ-U/TM alloys using the Md and the OOP as the alloying parameters. These results will assist the quantum design of nuclear fuel materials.

1. Introduction

Uranium alloys have been extensively investigated as fuels for next-generation nuclear reactors. Such alloys include low ^{235}U-enriched fuels used in research reactors, such as U_3Si_2–alminum (Al) dispersion fuel [1] and 10-wt% molybdenum (Mo) dispersed in an Al matrix [2,3]. Zirconium based U–Pu alloy is a promising fuel for advanced fast reactors [4].

Solid uranium has α (orthorhombic)-, β (tetragonal)-and γ (body centered cubic)- phases: which phase is present depends on the ambient temperature [5]. The α– and β–U phases form solid solutions with other metallic elements to a limited extent [5], whereas the γ-U phase readily forms solid solutions with other elements [5]. In addition, the α-U phase forms many intermetallic compounds with other metallic elements [6]. Accordingly, several α- and/or γ-U/transition metal (TM) alloys have been used in research nuclear reactors [7]. To produce advanced nuclear fuels, it is critical to understand the dissolution process of TM atoms into γ-U in terms of the constitutional diagram. Recently, some groups have theoretically studied the thermodynamic properties of U/TM alloys. Landa et al. studied the phase equilibria of U–Zr alloys, using the scalar-relativistic (i.e., without spin–orbit coupling) Green's function technique based on the Korringa–Kohn–Rostoker method [8]. They obtained good agreement between theoretical and experimental results for the ground-state properties of the γ- (bcc) and δ- (C32) phases of U–Zr alloys. Li et al. obtained the thermodynamic assessments of the Th–U and Th–Zr binary alloys and the Th–U–Zr ternary alloy, using the CALPHAD (calculation of phase diagrams) method based on experimental data that included the phase equilibria and thermodynamic properties of the alloys [9]. They found good agreement between the calculated phase equilibria and experimental data. Ab-initio calculations based on density-functional theory have also been used to examine the thermodynamic properties of U–Al systems [10,11]. To understand the dissolution of elements in solid U, in addition to obtaining the phase diagram or phase equilibria, it is also necessary to determine which electronic terms contribute to the thermodynamic properties of U alloys by employing density-functional theory in combination with experimental results.

We have previously investigated the alloying behavior of 3d-, 4d- and 5d-TMs in γ-U, using the discrete–variational Dirac–Fock–Slater (DV–DFS) molecular orbital (MO) method [12,13] which takes into account fully relativistic effects including spin–orbit coupling. We found that, with the exception of Ta and W, the maximum solid solubilities (MSS) of TMs in γ-U were exponentially proportional to both the d-orbital energy of the TM (Md) and the orbital overlap population (OOP) between the TM d

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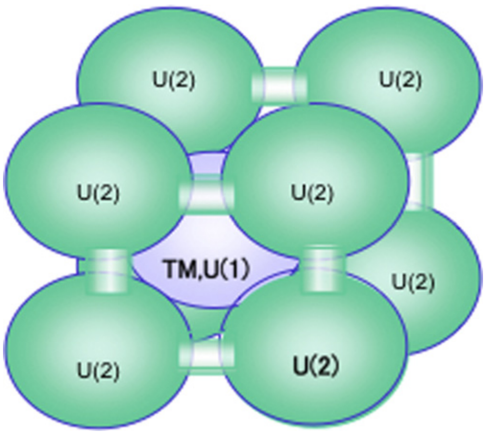

Fig. 1. Schematic representation of a cluster model for γ-U/TM alloys in which the central U atom is replaced by a TM atom in the unit cell of γ-U.

and U 6d atomic orbitals. The reason for this relation is not currently understood.

The aim of the present study is to clarify the reason for the exponential dependences of Md and OOP on the MSS. The MSS strongly depends on the thermodynamic equilibrium constant (K) that varies exponentially on the difference between the Gibbs free energies before and after substituting TM elements in γ-U. We discuss the dependence of the MSS on the Md and the OOP from a thermodynamic perspective.

2. Computational details

The DV–DFS MO method [14–16] is a powerful tool for studying the electronic structures of molecules containing heavy elements such as uranium [17–21]. The one-electron molecular Hamiltonian (H) in the DV–DFS MO method is written as:

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

where c is the velocity of light, P is the momentum operator, m is the rest mass of an electron, α and β are Dirac matrices, and $V(r)$ is the sum of Coulomb and exchange–correlation potentials. The MOs were obtained by taking a linear combination of atomic orbitals (AOs). Details of the DV–DFS MO method used in the present study are described elsewhere [14,22].

The basis functions, which are numerical solutions of the atomic DFS equations in an atomic-like potential, were obtained in the initial stage of iterations using a self-consistent procedure [23]. Thus, each basis function corresponds to an atomic orbital. The atomic-like potentials used for generating the basis functions were derived from the spherical average of the molecular charge density around nuclei obtained by adding a well potential (5.0 au in radius and −0.5 au in depth) for each atom. One-center (atomic) charges were estimated by Mulliken population analysis [24] in the self-consistent charge method [25] based on the self-consistent field approximation. All the DV–DFS MO calculations were performed with a Slater exchange parameter of 0.7 and with 18,000 DV sample points. The basis functions used were 1s–7p AOs for uranium, 1s–4s AOs for 3d TMs, 1s–5s AOs for 4d TMs, and 1s–6s AOs for 5d TMs. All the calculations were performed self-consistently until the difference between the orbital populations before and after an iteration became less than 0.01.

Morinaga et al. have demonstrated that the parameter Md is important when considering the alloying behaviors of metal alloys [26–30]. Md is defined to be a weighted average of the $d_{3/2}$ and $d_{5/2}$ orbital energies of the TM. The Md of the TM in γ-U/TM alloys and the U 6d orbital energy of U(1) (see Fig. 1) were evaluated by taking a weighted average of the $d_{3/2}$ and $d_{5/2}$ orbitals. The Md value was shifted relative to the Fermi level (E_F) of γ-U, which was used as a reference [26,27].

Since the bond overlap population (Bo) and the orbital overlap population (OOP), respectively, express the covalent bonding and interaction strengths between AOs, they have been often used to determine the contributions of individual AOs to covalent bonding [31]. We employed Mulliken population analysis to estimate the Bo and the OOP [24]. The Bo, $P_B(k,l)$, for a specific pair of atoms k and l in a polyatomic molecule is defined as:

$$P_B(k,l) = \sum_{(i)}\sum_{(r,s)} 2N_{(i)} C^k_{ir} C^l_{is} \left\langle \phi^k_r \middle| \phi^l_s \right\rangle , \tag{2}$$

where $N_{(i)}$ denotes the number of the electrons that occupy the ith MO and C^k_{ir} and C^l_{is}, respectively, represent the coefficients of the normalized AOs, ϕ^k_r and ϕ^l_s, in the linear combination of AOs for the ith MO. In a similar manner, the OOP, $P_O(k,r,l,s)$, for the ϕ^k_r and ϕ^l_s AOs is also defined as:

$$P_O(k,r,l,s) = \sum_{(i)} 2N_{(i)} C^k_{ir} C^l_{is} \left\langle \phi^k_r \middle| \phi^l_s \right\rangle \tag{3}$$

As described above, each basis function used in the present method corresponds to a specific AO, so that Eqs. (2) and (3) enable us to discuss the roles of individual AOs in the electronic structures and chemical bonding of molecules and condensed matters.

Fig. 1 shows a schematic representation of a model cluster for discussing the alloying behavior of TM atoms in γ-U. The central uranium atom [U(1)] is substituted by a TM atom. We used this model cluster for the following three reasons; (1) a similar small cluster consisting of nine U atoms reproduced the photoelectron spectra of solid α-phase U well [21]; (2) a similar small cluster consisting of one C and eight U atoms reproduced the photoelectron spectra of solid UC reasonably well [20]; (3) Morinaga et al. predicted the functional properties of metal alloys using such a small model cluster [30]. In addition, since the electrons in metal alloys

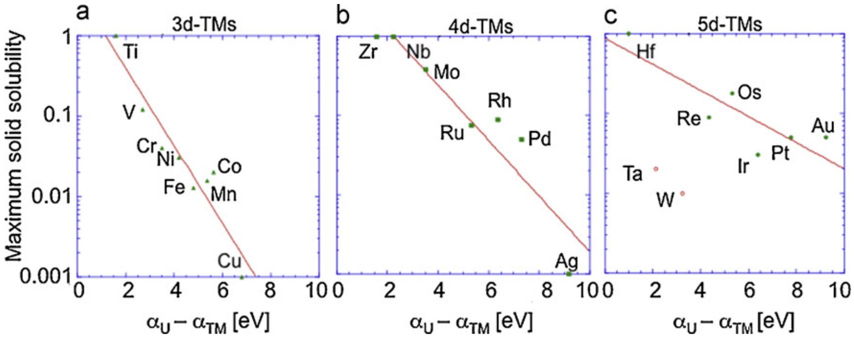

Fig. 2. Plot of the MSS as a function of the energy difference (α_U–α_{TM}) between the U 6d and TM d AOs.

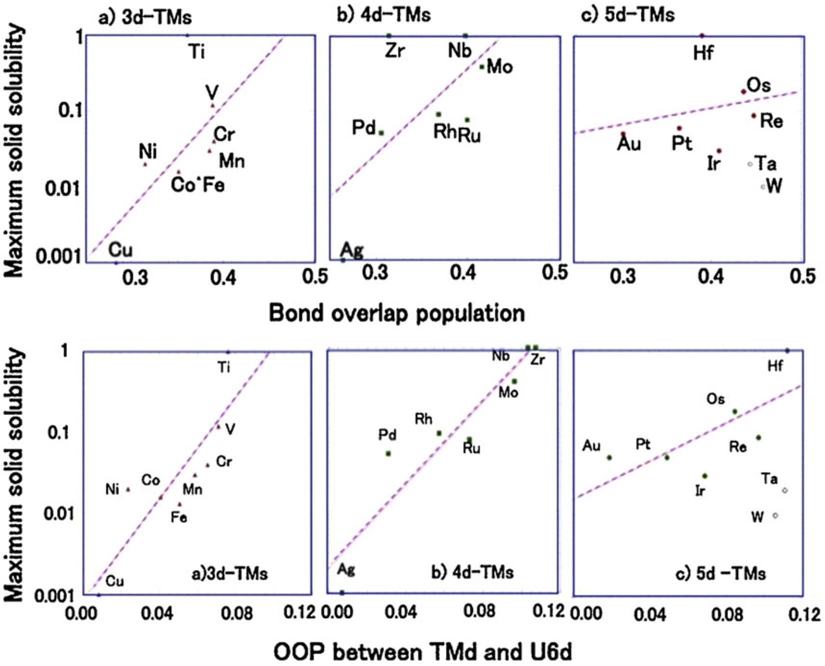

Fig. 3. Plot of the MSS as a function of the Bo (top) and the U 6d–TM d OOP (bottom: taken from Fig. 7 of Ref. [10]).

are not significantly polarized like ionic bonded crystals, it is not necessary to consider point charges surrounding the present model cluster.

To determine the differences in the electronic structures of the γ-U/TM alloys, the MO energy level structures and the chemical bonding of the γ-U/TM alloys were examined [13]. In the present study, lattice relaxation caused by the substitution of a TM atom was ignored because the values of Md and the OOP are not expected to be significantly affected by lattice relaxation [26–28]. The lattice constant of the model cluster was taken from the experimental value of 6.659 au for γ-U crystal [32].

3. Results and discussion

Fig. 2 shows a plot of the MSS as a function of the energy difference (α_U–α_{TM}) between the U6d and TMd AOs for γ-U/TM alloys. The energy difference (α_U–α_{TM}) is used to discuss charge transfer between U and TM atoms: it is an important parameter for quantum design of metal alloys [30]. Fig. 2 shows that the MSS exhibits an inverse exponential dependence on (α_U–α_{TM}), so that a smaller value of (α_U–α_{TM}) provides a larger MSS. Since the energy difference between the d orbitals is related to the magnitude of charge transfer between them, Fig. 2 implies that a smaller charge transfer between TM and U atoms gives rise to a larger MSS for γ-U/TM alloys.

Fig. 3 shows the correlation between the Bo and the MSS for γ-U/TM alloys (top), along with Fig. 7 of Ref. [10] showing the correlation between the TM d/U 6d OOP and the MSS (bottom). Although the Bo is thought to be a good parameter for predicting the physicochemical properties of metal alloys [26–30], the top of Fig. 3 indicates that there is a poor correlation between the Bo and the MSS. On the other hand, the bottom of Fig. 3 demonstrates the exponential dependence of the MSS on the OOP for all γ-U/TM alloys except those containing Ta and W. Thus, increasing the OOP increases the MSS of γ-U/TM alloys.

Figs. 2 and 3 reveal that the parameters describing the correlation between the TM d and U 6d AOs play an important role in determining the magnitude of the MSS of γ-U/TM alloys. In other words, the orbital interaction between the TM d and U 6d AOs is a

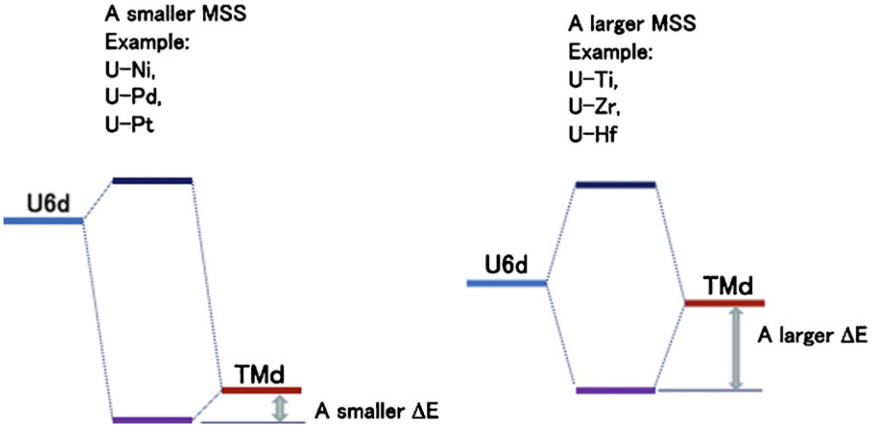

Fig. 4. Schematic illustration of the correlation between the MSS, the stabilization energy (ΔE), and the U 6d–TM d orbital energy difference (α_U–α_{TM}).

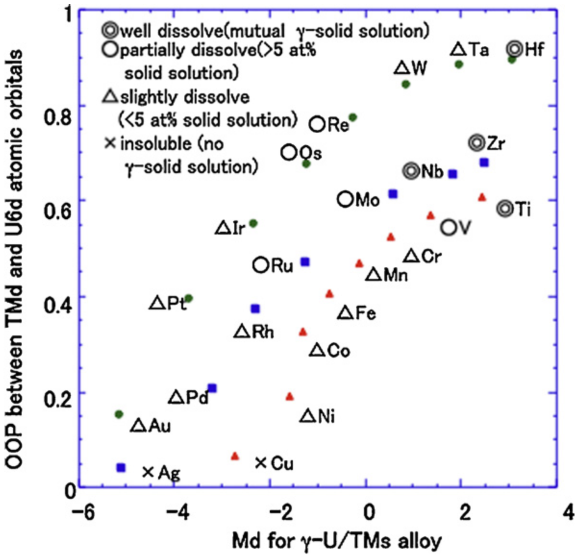

Fig. 5. OOP–Md plot for γ-U/TM alloys.

key parameter for estimating the MSS. We next discuss the physical effect of TM d/U 6d orbital interactions on the MSS.

Fig. 4 shows a schematic illustration depicting the relationship between the orbital interactions between the U 6d and TM d AOs based on the simple Hückel approximation [33] and the MSS. Using this approximation, the stabilization energy (ΔE) generated by the orbital interactions between the TM d and U 6d AOs can be expressed as:

$$\Delta E = \frac{1}{2}\left[\sqrt{(\alpha_{\mathrm{U}} - \alpha_{\mathrm{TM}})^2 + 4\beta^2} - (\alpha_{\mathrm{U}} - \alpha_{\mathrm{TM}})\right] \quad (\alpha_{\mathrm{U}} > \alpha_{\mathrm{TM}}), \tag{4}$$

where α_{U} and α_{TM} respectively denote the energies of the U 6d and TM d AOs; α_{U} is always greater than α_{TM} (see Fig. 4 of Ref. [12]). β expresses the resonance integral between them, which is proportional to the overlap integral (S) between the AOs and to the OOP. To discuss the correlation between ΔE and Md/OOP more clearly, we introduce the variables $t = (\alpha_{\mathrm{U}} - \alpha_{\mathrm{TM}})/2\left|\beta\right|$ and $F(t) = \sqrt{t^2 - 1} - t$ into Eq. (4). ΔE can then be rewritten as:

$$\Delta E = F(t) \cdot |\beta|. \tag{5}$$

By considering the ranges of the two quantities on the right-hand side of Eq. (5) (i.e., $t \geqq 0$ and $0 < F(t) \leqq 1$), we obtain:

$$0 < \Delta E \leqq |\beta|. \tag{6}$$

Accordingly, ΔE is a maximum (=$|\beta|$) when $F(t)$ is unity at $t = 0$. Thus, ΔE is maximized when $\alpha_{\mathrm{U}} = \alpha_{\mathrm{TM}}$. Conversely, ΔE becomes very small when the energy difference (α_{U}–α_{TM}) is much larger than unity ($\gg 1$). Consequently, a larger MSS for γ-U/TM alloys is obtained for a lower value of (α_{U}–α_{TM}) (corresponding to a larger ΔE), whereas a smaller MSS is obtained for a larger value of (α_{U}–α_{TM}) (corresponding to a smaller ΔE). This tendency can explain the results shown in Fig. 2. As Eq. (5) shows, ΔE also depends on $|\beta|$, which is proportional to the overlap integral S. Because the OOP increases with increasing S, ΔE also increases with increasing OOP. This tendency can also explain the result of Fig. 3 (bottom). Consequently, it can be concluded that the magnitude of ΔE generated by the interactions between TM d and U 6d AOs plays a key role in determining the magnitude of the MSS.

Why does the MSS vary exponentially with the Md [or (α_{U}–α_{TM})] and the OOP? We employed the present model cluster (see Fig. 1) as the basis for forming γ-U/TM alloys by substituting the central U atom with a TM atom. The following equilibrium has been considered using this model cluster:

$$\mathrm{U}_9 + \mathrm{TM} \Leftrightarrow \mathrm{U}_8\mathrm{TM} + \mathrm{U}, \tag{7}$$

where TM denotes a TM atom in the TM phase, whereas U_9/$\mathrm{U}_8\mathrm{TM}$ and U respectively denote a model cluster and an atom in the γ-U phase. When the equilibrium constant (K) of Eq. (7) increases, the concentration of $\mathrm{U}_8\mathrm{TM}$ increases, thus increasing the MSS. On the other hand, when K decreases, the $\mathrm{U}_8\mathrm{TM}$ concentration decreases, thus reducing the MSS. Consequently, the MSS is proportional to K. The MSS and K can then be written as:

$$\mathrm{MSS} \propto K = Ae^{-\Delta G/\mathrm{RT}}, \tag{8}$$

where A is a constant, ΔG denotes the Gibbs free energy difference before and after the substitution, R is the gas constant, and T is the absolute temperature. Since the lattice relaxation on substitution is negligible, the entropy is constant ($\Delta S = 0$) in the present substitution model. Thus, ΔG is equal to the enthalpy difference (ΔH) before and after the substitution. Accordingly, Eq. (8) can be expressed as:

$$MSS \propto K = Ae^{-\Delta G/\mathrm{RT}} = Ae^{-\Delta H/\mathrm{RT}}. \tag{9}$$

Since ΔH includes ΔE due to the TM d–U 6d orbital interactions, the following relationship is obtained:

$$MSS \propto K = Ae^{-\Delta H/\mathrm{RT}} \propto e^{\Delta E/\mathrm{RT}}. \tag{10}$$

As mentioned above, ΔE is proportional to both (α_{U}–α_{TM}) and S. Consequently, the MSS depends exponentially on both Md and the OOP.

Using Md and the OOP as parameters for determining the MSS, we examined the OOP–Md plot for γ-U/TM alloys. Fig. 5 shows the correlation map between the two parameters. Interestingly, γ-U/TM alloys with a lower MSS appear in the lower left of the OOP–Md map, whereas those with a higher MSS appear in the upper right. Thus, the map obtained using the OOP and Md is useful for designing γ-U/TM alloys. We believe that the present map can be used for other alloy systems besides the present alloy system.

4. Summary

We performed DV–DFS MO calculations for γ-UTM alloys. Md and the OOP (U 6d–TM d) exhibited good correlations with the MSS for γ-U/TM alloys. The magnitude of the MSS was explained based on the stabilization energy (ΔE) caused by U 6d–TM d orbital interactions for γ-U/TM alloys. The exponential dependence of the MSS on Md and the OOP was explained in terms of the equilibrium constant obtained using a substitution cluster model for γ-U/TM alloys. The OOP–Md plot is a good map for determining the MSS magnitude of γ-U/TM alloys. We believe that it can be used for other alloy systems besides the present alloy system.

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