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Electronic structure and magnetic properties of dilute U impurities in metals

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ABSTRACT

The electronic structure and magnetic moment of dilute U impurity in metallic hosts have been calculated from first principles. The calculations have been performed within local density approximation of the density functional theory using Augmented plane wave+local orbital (APW+lo) technique, taking account of spin–orbit coupling and Coulomb correlation through LDA+U approach. We present here our results for the local density of states, magnetic moment and hyperfine field calculated for an isolated U impurity embedded in hosts with *sp*-, *d*- and *f*-type conduction electrons. The results of our systematic study provide a comprehensive insight on the pressure dependence of 5*f* local magnetism in metallic systems. The unpolarized local density of states (LDOS), analyzed within the frame work of Stoner model suggest the occurrence of local moment for U in *sp*-elements, noble metals and *f*-block hosts like La, Ce, Lu and Th. In contrast, U is predicted to be nonmagnetic in most transition metal hosts except in Sc, Ti, Y, Zr, and Hf consistent with the results obtained from spin polarized calculation. The spin and orbital magnetic moments of U computed within the frame of LDA+U formalism show a scaling behavior with lattice compression. We have also computed the spin and orbital hyperfine fields and a detail analysis has been carried out. The host dependent trends for the magnetic moment, hyperfine field and 5*f* occupation reflect pressure induced change of electronic structure with U valency changing from 3^+ to 4^+ under lattice compression. In addition, we have made a detailed analysis of the impurity induced host spin polarization suggesting qualitatively different roles of *f*-band electrons on moment stability. The results presented in this work would be helpful towards understanding magnetism and spin fluctuation in U based alloys.

1. Introduction

Studies of the local electronic structure and magnetism of dilute impurities in metallic hosts form a mainstream in the investigation of magnetism. Especially, electronic structure calculations have played an important role in providing the basis for understanding the underlying mechanism in a more concrete way. In this regard, *ab initio* calculations based on density functional theory (DFT) have been quite successful in providing a basis for understanding various physical properties of solids. Many different methods developed over the years have been applied to dilute alloys of *d* and *f* impurities, successfully reproducing the experimental results observed for magnetic moment as well as hyperfine fields [1–21]. While, extensive experimental and theoretical studies have been carried out for 3*d*, 4*d* and 4*f* impurities [22–26], very little is known on the electronic structure and magnetism of dilute 5*f* impurities in metallic hosts.

It is well established that 3*d* and 4*d* impurities in metallic hosts show qualitatively different types of magnetism as compared to 4*f* impurities. While, 3*d* and 4*d* electrons forming broad energy bands are treated to be itinerant and their magnetic behavior is often described by an effective spin S_{eff}, most of the 4*f* impurities exhibit Hund's rule moment corresponding to the LS coupled ground state of a well defined ionic ground state. On the other hand, the 5*f* wave function of the actinides are more extended compared to 4*f* electrons and strongly hybridize with the ligand states resulting broad *f*-band near the Fermi energy. Depending on the strength of hybridization, the 5*f* electrons of actinides are often treated as being localized or itinerant. The interplay of localization and itinerant (delocalized) behavior of 5*f* electrons have given rise to many exotic phenomena like heavy fermion, non-Fermi liquid and quantum critical behavior, especially in U based alloys. In this context, a number of studies have been carried out in many U based inter-metallic alloys [22,27–34] to elucidate localization/delocalization of 5*f* electrons. Investigations of electronic structure and magnetism for dilute alloys with actinide impurities are useful to understand moment formation and the interaction of 5*f*

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electrons with different types of host conduction electrons. While, experimental studies for dilute actinide alloys are few because of limited solubility, theoretical investigations are practically non-existent. Such studies are necessary not only to understand the formation of local moment on 5*f* impurities in metallic hosts but also to examine the interplay of localization and delocalization of 5*f* electrons. To this end we have carried out systematic theoretical calculations for dilute U impurities in different metallic hosts. Here, we present our results for the electronic structure and magnetic moment of dilute alloys of U in *sp*, *d* and *f* band metals allowing a comprehensive understanding of moment formation and the influence of different types of host conduction electrons on the spin and orbital magnetism of the impurity atom. Based on Stoner analysis of the local density of states, we find that local moment formation is supported for U in most of the *sp*-metals including Cu, Ag and Au. On the other hand, U in *d*-band metals is predicted to be magnetic only in the early transition metals viz. Sc, Ti, Y, Zr, La, Th and Ce while, in all other transition metal hosts (V–Ni); (Nb–Pd) and (Ta–Pt) U is found to be nonmagnetic. The host dependent variation of the calculated magnetic moment, occupation number and hyperfine field reflect lattice compression induced change in the electronic structure of U with valency changing from 3^+ to 4^+. The large 5*f* band width combined with the observation of high orbital moment supports interplay of itinerant and localized behavior for U-5*f* electrons.

2. Computational details

The calculations presented in this paper have been performed within the framework of density functional theory [35–37], using the augmented plane wave+local orbital (APW+lo) method [37–39] as implemented in the WIEN2k package [40] to solve the Kohn–Sham equation [36]. In order to study the electronic structure of the U impurity a supercell of dimension $2\times2\times2$ of the basic unit cell was constructed using experimental lattice parameters [41]. The supercell with one of the host atoms substituted by U represents a dilute alloy with impurity concentration of 1/16 at%. For a few representative cases (Sc, Ti, Zn, In) calculations were also performed with a larger supercell ($3\times3\times3$) to examine possible impurity–impurity interaction. The inter-impurity distance in the supercells used for our calculations are large enough to ignore the effect of impurity–impurity interaction. In the APW+lo method, the unit cell is divided into two regions: (i) non-overlapping muffin-tin sphere of radius R_{MT} and (ii) remaining the so-called interstitial region. The wave functions within the atomic spheres are expanded in spherical harmonics and plane waves are used for the interstitial region. In our calculations we have used R_{MT}=2.1–2.4 a.u. for the host metals and 2.8 a.u. for U. The maximum multipolarity l of the wave function within the atomic sphere was restricted to l_{max}=10. The wave functions in the interstitial region were expanded as plane waves with a cutoff wave vector $K_{max}=7.5/R_{MT}^{min}=3.571$. The charge density was Fourier expanded up to $G_{max}=16\sqrt{Ry}$. For the exchange and correlation we have used the gradient corrected local density approximation (GGA) [42]. For sampling the Brillouin zone a dense *k*-mesh of size $10\times10\times10$ was used. For each of the cases lattice relaxation was adopted to minimize the force on each atom to less than 1 mRy/a.u. The self-consistency of the calculations are ascertained from the charge and energy convergence criterion set to be 0.0001 and 0.01 mRy respectively.

The spin and orbital contributions to the magnetic moment and hyperfine fields were extracted from spin polarized calculations using LSDA+U method taking account of the spin–orbit interaction and onsite Coulomb correlation, applying two schemes: (i) orbital polarization (OP) method developed by Brooks et al. [43,44] and (ii) mean field formalism of Anisimov et al. [45,46]. In OP method the Coulomb parameter U and the exchange integral J entering the energy functional are calculated self-consistently. This parameter free technique has been found to work well for *f*-electron systems as well as in strongly localized d ions e.g. Fe in alkali metal hosts [5,6,44,47,48]. However, in several other cases, especially in strongly correlated electron systems involving 4*f* and 5*f* electrons the OP method has been found to over estimates the orbital magnetic moment and the corresponding hyperfine field. The mean field approach on the other hand has been found to be successful in many cases. In this case the effective Coulomb energy $U_{eff}=U-J$ enters the energy functional as an external parameters. For our cases, we have taken U_{eff}=0.20 Ry consistent with the values reported from X-ray photo-emission (XPS) and Bremsstrahlung isochromat spectroscopy (BIS) measurements as well as recent theoretical calculations [49–51]. The spin and orbital moments as well as the hyperfine fields obtained from these calculations were found to be similar within accuracy limit.

Here we would like to note that because of the limitations of the LDA+U schemes adopted for our calculations, especially the different treatments of the onsite Columb interaction U_{eff} the calculated orbital magnetic moment may differ in magnitude. However, as will be discussed later, the uncertainty in U_{eff} does not alter the general trends observed for the magnetic moment and hyperfine fields which is the main focus of this study. We also like to add that in recent years several new methods have been developed to overcome the limitations of standard LDA+U approach to get more realistic description of correlated electron systems [52–54]. In particular, density functional theory combined with dynamic mean field theory (DFT+DMFT) have been found to be quite successful in providing improved understanding of band structure in strongly correlated 5*f* electron systems, especially Pu metal and its alloys [55,56]. To our knowledge DFT+DMFT method has not been applied extensively to study magnetism of dilute 5*f* impurities in metallic hosts except the case of Pu in Th [56]. A detailed study of 5*f* impurity magnetism in metallic hosts using DFT+DMFT method is beyond the scope of this work.

3. Results and discussion

Let us first discuss the results of the nonmagnetic (without spin polarization) calculations and examine the host dependent moment formation for U impurity. Formation of local moment on an impurity atom is governed by Stoner criterion $IN_l(E_F)>1$, where I is the Stoner parameter and $N_l(E_F)$ is the nonmagnetic local density of states at Fermi energy E_F for the impurity atom. Fig. 1 shows the projected local density of states (DOS) for U in different hosts. It can be noticed that in most of the *sp*-band hosts the U-5*f* DOS show a narrow peak near the Fermi energy reflecting the formation of a virtual bound state (VBS). In the case of *d*- and *f*-band metal hosts, the 5*f* VBS is observed for the early members of the series like Sc, Ti, Y, Zr, La, Th, Ce and Yb. The narrow 5*f*-width observed for most of the cases is consistent with weak crystal field splitting with magnitude $\lesssim$0.5 eV [57,58]. The host dependent change in the electronic configuration of U will be discussed in the later part of the paper. In most of the cases studied here except Ce and Yb, the U-5*f* VBS has little overlap with the host band electrons. For U in Ce and Yb, the impurity 5*f* VBS strongly overlaps with the host 4*f* band. Notice that with decreasing host volume i.e. lattice compression, the 5*f* peak of U become broader and shifts away from the Fermi energy. This is more clearly visible in transition metal hosts with 5*f* peak pushed above the Fermi energy for the hosts: V, Mo, Ru, Rh, Pd, Ta, W and Pt. The calculated U-5*f* local density of states at Fermi energy $N_l(E_F)$ are displayed in Fig. 2.