Mixed valency and site-preference chemistry for Cerium and its compounds: a predictive DFT study

Aftab Alam\textsuperscript{1,2} and D D Johnson\textsuperscript{1,3}

\textsuperscript{1}The Ames Laboratory, U.S. Department of Energy, Ames, Iowa, USA 50011-3020; \textsuperscript{2}Physics, Indian Institute of Technology – Bombay, Powai, Maharashtra, Mumbai, India 400076; and \textsuperscript{3}Materials Science & Engineering, Iowa State University, Ames, Iowa, USA 50011-2300.

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Cerium and its technologically relevant compounds are examples of anomalous mixed valency, originating from two competing oxidation states – itinerant Ce\textsuperscript{3+} and localized Ce\textsuperscript{4+}. Under applied stress, anomalous transitions are observed but not well understood. Here we treat mixed valency as an “alloy” involving two valences with competing and numerous site-occupancy configurations, and we use density functional theory with Hubbard U (i.e., DFT+U) to evaluate the effective valence and predict properties, including controlling valence by pseudo-ternary alloying. For Ce and its compounds, such as (Ce-La)\textsubscript{2}(Fe-Co)\textsubscript{14}B permanent magnets, we find a stable mixed-valent α-state near the spectroscopic value of $\nu_s = 3.53$. Ce valency in compounds depends on its steric volume and local chemistry; for La doping, Ce-valency shifts towards γ-like Ce\textsuperscript{3+}, as expected from steric pressure; for Co doping, valency depends on local Ce-site chemistry and steric volume. Our approach captures the key origins of anomalous valency and site-preference chemistry in complex compounds.

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Mixed valence compounds exhibit interesting anomalies when external parameters, such as pressure, are varied. Reliably predicting their properties and determining the origin of mixed valence effects remains open, and dependent upon correlating the properties with the molecular and crystal structure, and with local chemistry. Apart from the field of metallurgy and pigments in artwork and ceramics (e.g., Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{4})\textsuperscript{[1]} it also serves as an active area of research in complex biophysical problems, such as photosynthesis, and in organic-conjugated materials\textsuperscript{[2]} for artificial electronic devices.\textsuperscript{[3]} What makes these compounds different from other materials is the coexistence of wide s-d bands and very heavy atomic-like f-electrons at/near the Fermi energy. Anomalous properties then arise from a competition between the itinerant and localized nature of the f-electrons. Numerous experiments have revealed a growing list of such compounds from the rare-earth (RE) series, the actinides, and with local chemistry. Apart from previous work\textsuperscript{[5–8]} on rare-earth systems using model Hamiltonians,\textsuperscript{[9]} and consistent with a correlated and multi-electron picture of Ce with semi-isolated 4f states in contact with a bath of spd valence electrons, as found experimentally.\textsuperscript{[10]}

Addressing mixed valency using a density functional theory (DFT) treats magnetism, atomic multiplet effects, and crystal field splitting on an equal footing, and identifies the electronic mechanisms responsible for the anomalous valence behavior. While a first-principles Dynamical Mean-Field theory (DMFT) may better describe the fluctuating mix valency, our approach captures the key effects in complex compounds with dramatically less computational intensity. Notably, within DMFT $\delta$-Pu is found to be a superposition of two atomic valences (60\% $f^5$ and 40\% $f^6$).\textsuperscript{[3]} Yet, experimentally, $\alpha$ and $\delta$ Pu have a superposition of three 5$f$ states\textsuperscript{[2]} ($\sim$ 20\% $f^4$, 40\% $f^5$ and 40\% $f^6$), a ternary “alloy” (2 independent fractions).

We use Vienna \textit{ab-initio} simulation package VASH\textsuperscript{[10]} with a pseudopotential and projected-augmented-wave basis\textsuperscript{[11]} using Perdew-Burke-Ernzhof (PBE) exchange correlation and spin-orbit coupling. With different sized Ce\textsuperscript{3+} and Ce\textsuperscript{4+} ions, relaxations – ignored in previous studies – are crucial to predict reliable energetics and groundstates. Localized Ce\textsuperscript{3+} f-electrons are addressed via a PBE+U approach\textsuperscript{[12]} with a Hubbard U (set to 5 eV from previous work\textsuperscript{[13]}) introduced in a screened Hartree-Fock manner. See footnote for more details.\textsuperscript{[14]}

The formation enthalpy $\Delta E$ and volume $V$ versus Ce-
valence in fcc Ce mixed-valence “alloys” are shown in Fig. [1]. Here Ce$^{3+}$ and Ce$^{4+}$ potentials are occupied over 8 sites in a Ce supercell to find the energetically most favorable configuration; hence, we have discrete jumps of 0.125 valence “composition”. From Fig. [1] the energetically most favorable mixed-valence state occurs near 3.5 (a 5th-order polynomial fit yields $\nu_s = 3.55$), near the assessed value of 3.67. We find that the mixed valence $\alpha$-state of Ce arises from a energetically favorable distribution of the two Ce$^{3+}$ and Ce$^{4+}$ states. (Using more sites fills in the curve, needed in skewed distributions.) Atomic positions and the cell volumes are fully relaxed in each data. The relaxed, DFT+U calculated $V_s$ are compared with known experimental volumes [13] (red squares), and are within 8% and have the correct trend for the $\gamma$, $\alpha$ and $\alpha'$ phases. For pure Ce, the mixed-valency corresponds to a volume between those of purely $\gamma$- and $\alpha$-phase. Including the on-site U for Ce$^{3+}$ (with 4f-electron) and the spin-orbit coupling is important to get the correct groundstate for the intermediate valency.

Next, we investigate the Ce mixed valency in Ce$_2$Fe$_{14}$B, a challenging 68-atom per cell, tetragonal structure with space group P4$_2$/mnm. Mixed valency of Ce significantly affects its magnetic behavior. Due to the complex nature of 2-14-1 structure [3] the Ce mixed valency is associated with Ce site preferences. The 2-14-1 structure contains two inequivalent rare-earth (R) sites – R(4f) and R(4g) – each with multiplicity 4 [13]. From the co-ordination shell around each site, 4g-sites acquire a larger volume than 4f-sites. As such Ce$^{3+}$ (larger ion) prefers to occupy the 4g-sites while Ce$^{4+}$ (smaller ion) the 4f-sites. Energetically favored configurations are found by mixing Ce$^{3+}$ and Ce$^{4+}$ on the 8 R-sites in all possible ways.

The formation energy gain/loss $\Delta E$ versus Ce valence in (Ce$^{3+}$-Ce$^{4+}$)$_2$Fe$_{14}$B for all 8 R-site configurations are shown in Fig. [2]. The filled circles indicate energies when Ce$^{3+}$ is favorably distributed over 4g-sites and Ce$^{4+}$ on 4f-sites; filled squares are the results with the opposite (unfavorable) distribution of Ce-ions. Other symbols indicate intermediate sets of distribution where 3+ and 4+ ions are mixed over both the sites with a binomial distribution. Notice the asymmetric nature of the energy curves comparing the lower vs. upper half of $\Delta E$, which is due to a different filling on the 2 inequivalent RE-sites; that is, the collective effect of filling Ce$^{3+}$ ions preferentially over 4f-sites are very different from that of 4g-sites. The favorable mixed-valency occurs near $\nu_s = 3.5$ (3.55 from polynomial fit), near the assessed 3.44 [14].

To improve magnetic properties requires engineering Ce- or Fe-sites in such a way to push the Ce-valency either towards 3+ or 4+. Due to the dependence of Ce-valence on the steric volume [3], one way to manipulate the Ce valency is to vary the unit cell volume by forming pseudo-ternary compounds. We studied two compounds, i.e., (Ce,La)$_2$Fe$_{14}$B and Ce$_2$(Fe,Co)$_{14}$B; the former (later) should increase (reduce) the unit cell volume. First, we dope RE Ce-sites by La in Ce$_2$Fe$_{14}$B. Out of the two inequivalent RE sites 4f and 4g, La (being larger than Ce) prefers to occupy the 4g sites. Figure [3] shows $\Delta E$ vs. Ce valence with 12.5% of La doping (1 out of 8 sites) in Ce$_2$Fe$_{14}$B. From the data in the vicinity of the minimum ($x \sim 3.5$), La-doping clearly moves the Ce-

FIG. 1. (Color online) (Top) Relaxed volume (Bottom) formation enthalpy vs. Ce valence for pure fcc Ce where trivalent (3+) and tetravalent (4+) Ce are mixed. Square symbols indicate experimental volume (from Ref. [10]). Vertical dashed line is just a guide to the eye for the estimated minimum.

FIG. 2. (Color online) Mixed valency of Ce in Ce$_2$Fe$_{14}$B. Black (blue) curve indicates the formation enthalpies of mixing Ce$^{3+}$ and Ce$^{4+}$, with the larger 3+ ions distributed over 4g (4f) sites and smaller 4+ ions over 4f (4g) sites. Star and triangles indicate the energies for intermediate sets of distribution where 3+ and 4+ ions are mixed over both the sites.
valency towards 3+ relative to the undoped case. This effect is in accord with the steric volume argument: a La-ion, being larger than Ce, expands the lattice when doped in Ce₂Fe₁₄B, enhancing the steric volume of Ce site(s) and supports a more trivalent-like state. Steric volume is an important factor controlling the Ce chemical valence, as also evidenced in hydrogenated Ce₂Fe₁₄B and Ce₂Fe₁₇ compounds.[13,19]

Next, we study the effects of Co doping on Fe-sites in Ce₂Fe₁₄B, which is known that to enhance the Curie temperature and magnetic anisotropy and, hence, a reason for our choice. Ce₂(Fe,Co)₁₄B crystallizes in the same P₄₂/mmm structure as Ce₂Fe₁₄B, which has six inequivalent Fe-sites, i.e., Fe(k1), Fe(k2), Fe(j1), Fe(j2), Fe(e) and Fe(c). First we verified the Co site preference on these symmetry distinct Fe-sites. Figure 4 (top) shows the site-preference energy for both Ce³⁺ and Ce⁴⁺ when 1 out of 14 Fe-sites are doped with a Co atom. Results indicate that Fe(j2) site has the strongest preference for not occupying Co, as it costs the highest energy.

This finding is supported by two arguments: (1) Co and Fe differ a little in size (R₁₄ < R₄), out of 6 Fe-sites in 2-14-1, Fe(j2) has the largest coordination volume – a reason for Co to avoid j2-sites. (2) j2-sites in 2-14-1 and C(dumbbell)-sites in rhombohedral Ce₂Fe₁₇ structure[13] are reported to be crystallographically, as well as magnetically, cognates. In other words, each of these sites have the largest number of near-neighbor Fe-ions and the largest moment. Also, these sites are the only transition-metal sites that have a major ligand line – perhaps another reason behind the unfavorability of Co to occupy j2-sites. Fe(c) and Fe(j1) sites have the strongest preference towards Co. This site preference can be justified from the large affinity of Co towards rare-earth, i.e., those transition-metal-sites that acquire the highest RE-coordination will prefer to have Co on it. Fe(c) and Fe(j1) indeed has the highest coordination of RE around it.

Figure 4 shows ∆E vs. Ce valence for Ce₂(Fe₁₃Co)B with Co doped on the energetically most favorable Fe(c) site. Unlike Ce₂Fe₁₄B (Fig. 2), 7.14% Co doping (1 out of 14) already favors the mixing of Ce valence at the Ce⁴⁺ end, i.e., no positive (unfavorable) ∆E. Again, compared to the Ce valence in Ce₂Fe₁₄B, Co doping pushes the valency of Ce towards 3+ (similar argument about the location of minima holds in this case). This, however, does not jibe with the volume argument used for La doping. Co being smaller than Fe leads to a volume reduction that should move the Co valence towards 4+ via steric effect. Again, compared to the Ce valence in Ce₂Fe₁₄B, Co doping pushes the valency of Ce towards 3+ (similar argument about the location of minima holds in this case). This, however, does not jibe with the volume argument used for La doping. Co being smaller than Fe leads to a volume reduction that should move the Co valence towards 4+ via steric effect. This finding is supported by two arguments: (1) Co and Fe differ a little in size (RCo < RFe), out of 6 Fe-sites in 2-14-1, Fe(j2) has the largest coordination volume – a reason for Co to avoid j2-sites. (2) j2-sites in 2-14-1 and C(dumbbell)-sites in rhombohedral Ce₂Fe₁₇ structure[13] are reported to be crystallographically, as well as magnetically, cognates. In other words, each of these sites have the largest number of near-neighbor Fe-ions and the largest moment. Also, these sites are the only transition-metal sites that have a major ligand line – perhaps another reason behind the unfavorability of Co to occupy j2-sites. Fe(c) and Fe(j1) sites have the strongest preference towards Co. This site preference can be justified from the large affinity of Co towards rare-earth, i.e., those transition-metal-sites that acquire the highest RE-coordination will prefer to have Co on it.

It is well known that Co has a strongly affinity to RE elements (Ce in this case), as such Ce favors a high coordination number of Co. In 2-14-1, Fe(c) sites with 4 Ce and Fe(j1) sites with 3 Ce have the highest number of RE neighbors. These Fe-sites are indeed the energetically most favorable site for Co, see Fig. 4 (top). Now, because RCo < RFe, the accumulation of a large number of Co around Ce-site causes the formation of major ligands, given by lines connecting faces of Voronoi polyhedra, allowing more room and an expansion of the local Voronoi volume around the Ce-site. (These Voronoi polyhedra
and volumes were determined by inscribed radii given by saddle-points in the electronic density.\(^2\) Note how the central Ce-polyhedra expands (Fig. 5) due to Co-doping on Fe-sites. Thus, although Co doping reduces the unit cell volume, the local steric volume around the Ce-site is enhanced which shifts the Ce valency towards 3+. This phenomenon is based on the local chemistry and the nature of hybridization with neighboring atoms, instead of the simple volume argument alone.

In summary, we have presented an “alloy” approach to predict reliably the mixed-valency properties in complex compounds, for which DFT+U methods are essential, and reveal the electronic origin for such behavior. For Ce-based materials, cerium does not have a well-defined valence; rather its f-electrons fluctuate between two extreme valence states dependent upon local atomic configurations (site occupancy) with a distributions of 3+ and 4+ Ce. The energy difference between these states/configurations is a few meV-atom\(^{-1}\), so associated anomalies are observed, e.g., under pressure. The mechanism for such a transition and the reason for differing valence states was not yet well understood. Doping puts the material under an chemical pressure – La doping at Ce sites expands the lattice (as expect from steric volume arguments), while a transition-metal dopant like Co at Fe sites shrinks it (in contrast to steric volume arguments). Here we predicted the mixed valency of Ce in pure Ce and Ce\(_2\)Fe\(_{14}\)B, in agreement with experiment; then, we addressed two different types of doping (La at Ce-sites and Co at Fe-sites) to reveal how both steric volume and local chemistry influence the Ce valence in compounds, reflected in the nature of hybridization with neighboring atoms, i.e., Ce site preferences arising from the large electron affinity of Co towards rare-earth elements.

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*Emails: aftab@ameslab.gov (aftab@phy.iitb.ac.in); ddp@ameslab.gov

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