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Physical properties of the 6*d*-series elements from density functional theory: Close similarity to lighter transition metals

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We have calculated some of the physical properties of the recently discovered 6*d* elements by density functional theory. Comparison with those of the 5*d* metals shows that there is a close analogy for the crystal structures, for parabolic variation of equilibrium atomic volumes and bulk moduli, and an almost linearly increasing behavior of the pressure derivative of the bulk modulus across the 6*d* series. The Friedel model that is used to explain these trends for homologous series also holds for 6*d* metals. These elements also seem to be placed correctly in the Periodic Table.

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The nonmagnetic transition-metal 4*d* and 5*d* series show a systematic trend in their cohesive properties as the number of *d* electrons increases across a given series. These elements display a parabolic-like change in ambient pressure equilibrium atomic volumes with a progressive increase in *d* electrons. This was attributed by Friedel[1] to the filling of *d* bonding states in the beginning of each series and then antibonding states from the middle of the series on. The following expression was given for the contribution of the *d* electrons to the cohesive energy:

$$E_{\mathrm{coh}}(N_d) \approx -1/2 W_d N_d (1 - N_d/10),$$

where N_d is the number of *d* electrons and W_d is the width of the *d* band. This expression shows that the chemical bonding reaches a maximum for a half-filled *d* band and varies as $(N_d)^2$. Also, Pettifor[2] showed that there is an inverse relationship between the atomic volume and the cohesive energy, and hence the parabolic behavior for atomic volumes follows. This parabolic-like behavior of atomic volumes is regarded as an indicator of the itinerant character of electrons, and it is often used to draw analogies for other groups such as early actinides. The bulk modulus, as expected, shows an inverse behavior. It first increases up to the middle of a series and then decreases. The pressure derivative of the bulk modulus exhibits almost a linear trend. This has been related by Vohra *et al.*[3] to the variation of $s \leftrightarrow d$ electron transfer parameter across these elements. The crystal structures adopted also show a systematic trend: hcp-bcc-hcp-fcc from Lu to Au in the 5*d* elements.

The following question now may be asked: will the 6*d* transition elements ($Z = 103$–111), which form part of the recently completed seventh period of the Periodic Table, follow these systematics? These elements are short-lived and no physical property measurements have been carried out so far. This is due to the lack of a sufficient amount of samples of these elements. On the other hand, a few chemical properties of some of these post actinides have been investigated. The results are still controversial and indicate that, chemically, they may be different in some aspects from their lighter homologues in the same column of the Periodic Table.[4] This may hold for cohesive properties as well. One can now employ theoretical methods such as first-principles density functional theories (DFT) for total energy calculations to answer such questions. It is now well established that such theoretical determinations give reliable results. We have followed this approach here. Comparison shows that the trends in the physical properties of the 6*d* transition series follow the earlier series almost perfectly, and there are no surprises. These results are described in this paper.

All the required total energy calculations have been performed at 0 K by the full- potential linearized augmented-plane-wave (FP-LAPW) method as implemented in the WIEN2K package.[5] The exchange correlation part of the total energy was evaluated using the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA) incorporating scalar-relativistic (SR) effects.[6] Spin-orbit (SO) effects were not considered in these first-generation calculations on these elements. In this regard, our approach is similar to that of Noffsinger and Cohen.[7] We will provide some justification for this below and show that in Rf ($Z = 104$), the volume difference between the SR and SR + SO calculations is only 1.5%. For each element, the 7*s*, 7*p*, and 6*d* states were treated as conduction states while the 5*f*, 6*s*, and 6*p* electrons were included as semicore states. A grid of 8000 *k* points was used for sampling the Brillouin zones. The plane-wave cutoff parameter $R_{\mathrm{MT}}\ K_{\max}$ was fixed at 9 with muffin-tin radius R_{MT} chosen to be 2 a.u. for the whole series. The self-consistent cycle in each case was run until the energy convergence criterion of 0.01 mRy was met. The computations have been done for hcp, bcc, and fcc structures for all elements except for Rf ($Z = 104$), where the three-atom hexagonal ω structure[8] was also included as it occurs for the same group elements, Ti, Zr, and Hf, under pressure. For consistent comparisons, we also carried out computations for all the 5*d* transition elements. We have used the Birch-Murnaghan equation, available in the WIEN code, to derive the equilibrium volume (V_0), the bulk modulus (K_0), and its pressure derivative (K_0'). However, cohesive energies are not given, as the usual FP-LAPW calculation in the WIEN code does not give a correct estimation of this parameter for heavy elements.

We have done structure optimizations for all the 6*d* elements. As an example, Fig. 1 illustrates total energies of Rf in bcc, fcc, hcp, and ω structures. It clearly demonstrates that hcp is the lowest-energy structure, in agreement with the

TABLE I. Equilibrium properties for 6*d* and 5*d* transition elements. c/a values: Lr (1.55), Rf (1.58), Bh (1.61), and Hs (1.58).

	6*d*-theoretical						5*d*-theoretical[b]			5*d*- experimental[c]		
	Optimized structure	V_0 (Å^3)	Density[a] (gm/cc)	K_0 (GPa)	K_0'		V_0 (Å^3)	K_0 (GPa)	K_0'	V_0 (Å^3)	K_0 (GPa)	K_0'
Lr	hcp	30.3	14.4	42	3.33	Lu	29.0	47	3.26	29.4	41	
Rf	hcp	24.6	17.9	96	3.75	Hf	22.5	107	3.44	22.2	109	3.95
Db	bcc	20.6	21.6	177	3.93	Ta	18.3	194	3.78	18.0	200	3.79
Sg	bcc	18.6	24.2	279	4.13	W	16.1	305	4.05	15.8	323	4.33
Bh	hcp	17.4	26.0	345	4.37	Re	15.0	367	4.22	14.7	372	5.41
Hs	hcp	16.7	26.9	388	4.74	Os	14.3	400	4.59	14.0	418	3.40
Mt	fcc	16.8	27.3	353	5.08	Ir	14.5	350	4.92	14.2	355	4.83
Ds	fcc	18.1	25.7	258	5.41	Pt	15.6	248	5.34	15.1	278	5.18
Rg	bcc	20.9	22.4	132	6.29	Au	18.0	139	5.89	17.0	173	6.29

[a] The atomic weights were taken from the compilation by NIST.[8]

[b] For 5*d* series, the experimental structures were assumed.

[c] V_0 and K_0 values are from Ref. 9, and K_0' are based on sonic velocity measurements, taken from a compilation by Raju *et al.*[10]

experimental data of the lower *d*-series elements of this group. The other members of the 6*d* series, except for Rg, are also found to exist in the corresponding crystal structures of the 5*d* elements with metallic character (see Fig. 5 below). These are listed in Table I along with other equilibrium parameters. For comparison, the computed values for 5*d* series are also given. The values for these are in very good agreement with experimental data,[9,10] also shown in the table. The solid densities were evaluated from the atomic weights quoted by NIST.[11]

It is interesting to note that atomic volumes are expanded from those of the 5*d* elements. It was pointed[12] out earlier that there are enhanced relativistic effects in the seventh period of the Periodic Table, due to which the *d* orbitals are expanded. The atomic radii of *trans*-actinides, deduced from theoretical and experimental studies of the chemical compounds of these elements, are about 0.05 Å larger than those of the 5*d* elements.[13,14] Our present results are in agreement with this. Similar expansions have been found by DFT methods for solid Eka-Hg ($Z = 112$) compared to Hg[15] and for solid Uuq ($Z = 114$) compared to Pb.[7,16] It may also be noted that for Eka-Hg, different relativistic treatments do not lead to much change in atomic volumes, 25.87 Å^3/atom versus 25.79 Å^3/atom for scalar and four-component relativistic formalisms, respectively, for the hcp structure. To further confirm this, we also have done an SR + SO calculation on hcp Rf. The equilibrium volumes for the two computations are 24.60 and 24.28 Å^3/atom, respectively.

The trend in the volume expansions of the earlier *d* series is $5d \approx 4d > 3d$. It may be argued that the very small volume change between the corresponding 4*d* and 5*d* elements is because of the rare-earth contraction, and therefore the 5*d*-6*d* expansions should follow the 3*d*-4*d* behavior. However, this view is contrary to the cancellation theorem of Heine.[17] According to this, the 3*d* electrons are relatively tightly bound as there are no $l = 2$ core states to weaken the ionic potential seen by them. In 4*d* series, however, the situation is different as 3*d* electrons would screen the potential and lead to volume

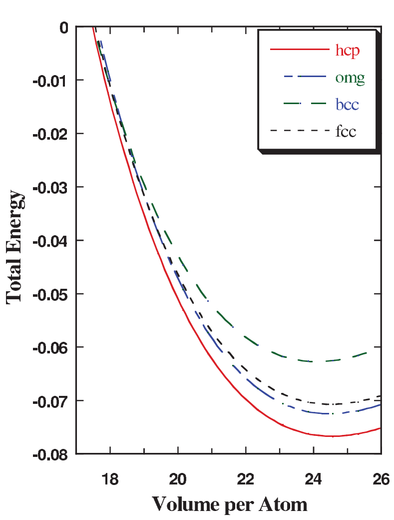

FIG. 1. (Color online) Relative energy (Ry/atom) as a function of volume (Å^3) for Rf in hcp, ω (omg), bcc, and fcc structures.

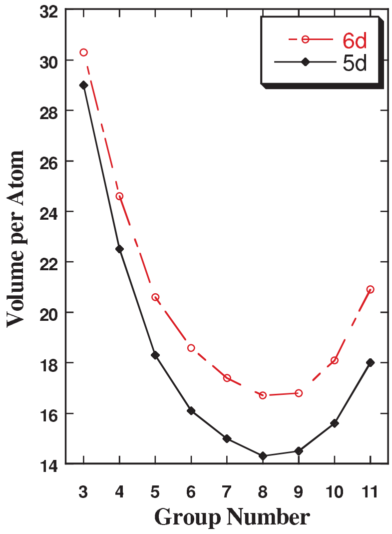

FIG. 2. (Color online) Comparison of equilibrium atomic volumes (Å^3) across the 6*d* and 5*d* transition-metal series.

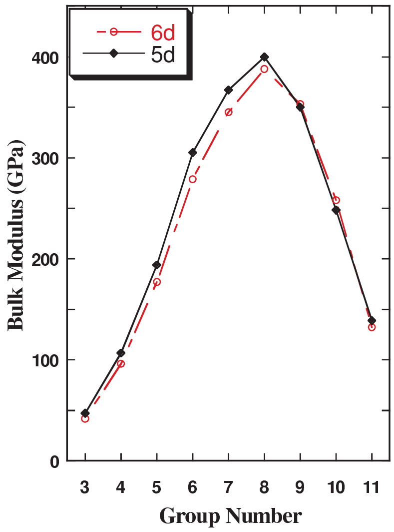

FIG. 3. (Color online) Comparison of bulk moduli across the 6*d* and 5*d* transition-metal series.

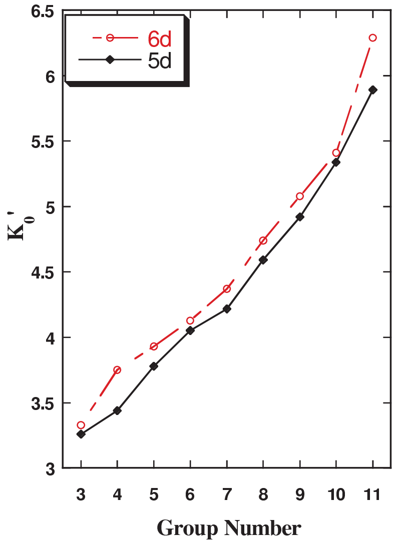

FIG. 4. (Color online) Comparison of pressure derivative of bulk modulus (K_0') across the 6*d* and 5*d* transition-metal series.

expansion. Further, Heine notes that "one core shell already does a lot of cancellation and there is no dramatic change for more than one." This is what holds for the 5*d*-series volumes. This should also be applicable for 6*d* elements, and therefore the cause for 5*d* to 6*d* expansion does not seem to be related to 3*d*-4*d* behavior.

Figures 2, 3, and 4 illustrate the trends in V_0, K_0, and K_0', respectively, across the 6*d* and 5*d* series. It may be noted that

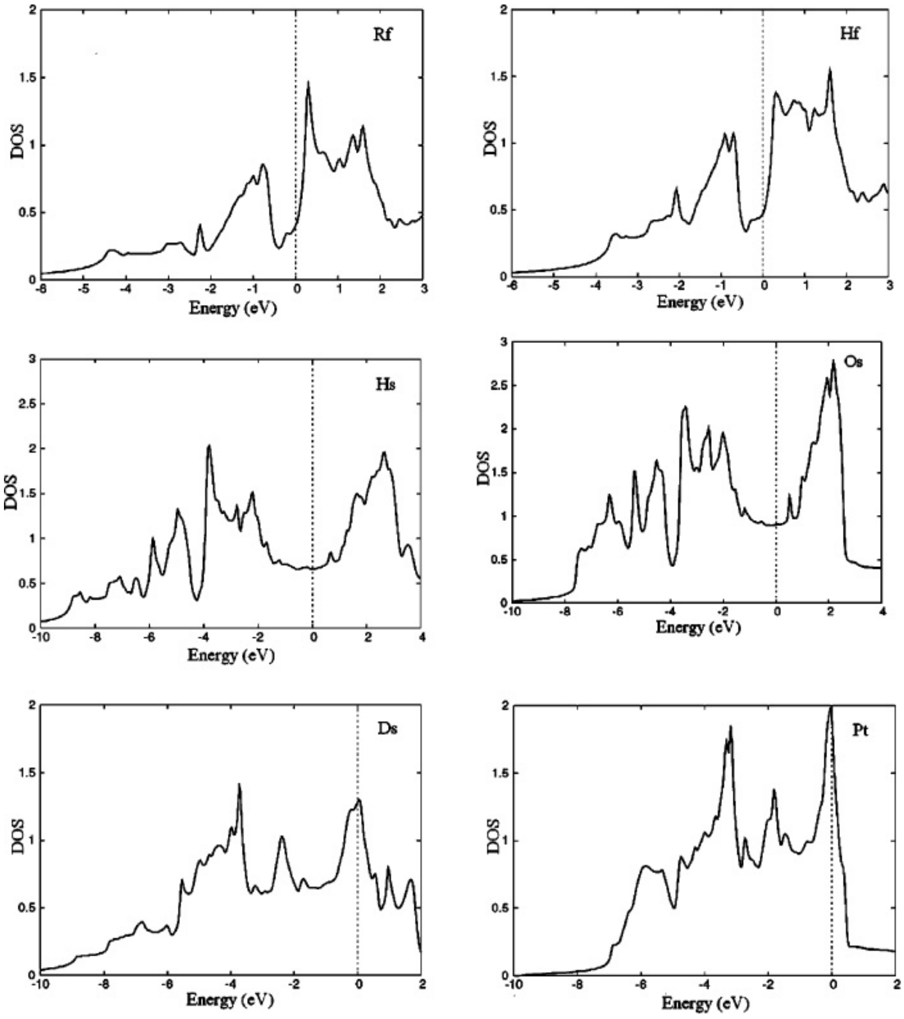

FIG. 5. Density of states (DOS) in states/eV of Rf, Hs, and Ds compared to Hf, Os, and Pt. The line at zero energy indicates the Fermi energy.

there is a close similarity. Some differences in the K_0' values may be due to the inadequacy of the BM equation used for fitting equation-of-state parameters, as recently pointed out by Qin *et al.*[18] The calculated solid densities are increased by 20% to 30% with respect to the corresponding 5*d* solids, and they will be highest among all known elements. The densities of states for Rf, Hs, and Ds are compared with corresponding 5*d* metals Hf, Os, and Pt in Fig. 5. The densities of states are dominated by *d* states. The *d* states in all cases are split into two parts: bonding half and antibonding half connected by a region of flat density of states. In Rf (Hf), there is only partial occupancy of the bonding states. In Hs (Os), lying in the middle of the series, the lower part of the *d* band is full, and in Ds (Pt), both parts of the *d* bands are occupied. This implies that the known physical picture of transition-metal bonding as specified by Friedel can be directly transferred to 6*d* metals.

Due to increased relativistic effects expected in post actinides, many authors[4,13,15] have raised doubts about the similarity of their properties with lighter homologues and hence their correct placement in the corresponding group in the Periodic Table. At the present level of treatment of relativistic effects, we find no evidence of this from the data on the physical properties generated in this paper.

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