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CHEMICAL PHYSICS OF HEAVY ELECTRON URANIUM COMPOUNDS

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Summary

We discuss chemical trends relating to the formation of heavy electron compounds by uranium.

1. Introduction

At low temperature the specific heat of metals varies with temperature as $C = \gamma T + \beta T^3$. β is proportional to the inverse cube of the Debye temperature and γ, the electronic specific heat coefficient, is proportional to the electronic density of states at the Fermi level. Simple metals such as copper and gold have $\gamma \approx 1$ mJ mol^{-1} K^{-2}; transition metal elements (and their metallic compounds) can have $\gamma \approx 10$ mJ mol^{-1} K^{-2}. The largest γ known for an element is that of stabilized δ-Pu, for which $\gamma = 55$ mJ mol^{-1} K^{-2} [1]. In the progression from sp to d to f elements we can find examples with ever increasing γ due, we believe, to the increasing contribution of the more localized electrons to the density of states at the Fermi level. Put another way, d and f electrons tend to form narrower bands.

It is now known that a number of the intermetallics formed by the f elements cerium, ytterbium, uranium and neptunium have substantially larger γ, and these γ are temperature dependent and increase on cooling past a temperature typically near 4 K. The γ for these compounds are generally defined per mole of f element, since to date only f-element compounds show the upturn, thus making it reasonable to assume that the f electrons are somehow responsible for the heavy electron behavior reflected in the large γ. It is the upturn in C/T that is used to characterize the heavy electron materials and this, as far as is known, only occurs for γ in excess of 150 mJ (mol f)$^{-1}$ K^{-2}.

There is a useful, qualitative way to think about these heavy electron materials. At high temperature (above about 100 K) they have a Curie–

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Weiss-type magnetic susceptibility, with effective moments close to that expected for the Hund rule ground state of the f configuration. This susceptibility χ goes over at low temperature into a Pauli-type susceptibility which is characterized by lack of saturation in M *vs.* H for large H/T. Both γ and χ are proportional, within the free electron theory of metals, to the electronic density of states at the Fermi level, and it is interesting that most of this density of states determined from $\chi(T = 0)$ shows up in $\gamma(T = 0)$ (Fig. 1). We can view this development of a Pauli-type susceptibility as a loss of the high temperature local moment because of interaction between the conduction and f electrons. The entropy associated with the local moment degeneracy at high temperature must show up in the conduction electron system at low temperature. If the f ground state has spin J, the entropy involved is $R \ln(2J + 1)$ per mole, and if the temperature characterizing the loss of this local moment entropy is T_0, then we estimate $\gamma \approx R \ln(2J + 1)/T_0$. For a doublet and $T_0 = 10$ K, we get $\gamma \approx 576$ mJ (mol f)$^{-1}$ K^{-2}.

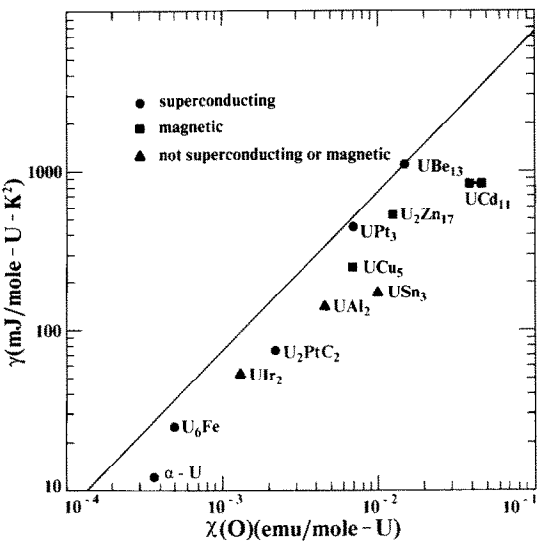

Fig. 1. Ln $\gamma(0)$ plotted against ln $\chi(0)$ for selected compounds. The line gives the free-electron relationship between γ and χ.

Chemically ordered heavy electron compounds then establish a so-called "coherent" state in the conduction electrons at low temperature from what is essentially a collection of independent magnetic ions at high temperature. This viewpoint is also supported, it turns out, by the rather large characteristic variation with temperature seen in the Hall constant, which can be interpreted within this framework. These variations in the Hall constant also occur in some f materials with γ below 150 mJ (mol f)$^{-1}$ K^{-2}, and this suggests that there may be a smooth continuum of physics from low γ to high γ.

2. Occurrence of heavy electron materials

We restrict our attention to the intermetallics of uranium. The first point to make is that all the heavy electron uranium materials are beyond the Hill limit in the Hill plot (Fig. 2), namely in the magnetic limit. Additionally, the metallic radius of uranium in the heavy electron compounds is, where it is possible to make comparisons with corresponding rare earth intermetallics, large and close to the metallic radius of gadolinium. The "light" electron uranium compounds have metallic radius close to that of erbium.

It is also informative to notice where the elements that form heavy electron binary compounds with uranium lie in the periodic table (Fig. 3). What we see is that the heavy electron binaries form near the boundary between the d elements and sp elements. There are no compounds of interest to us on the left-hand side of the table (noting the shifting of beryllium and magnesium that we have made) at the other sp–d boundary, because uranium does not form any compounds here. Moving to the right of the heavy electron materials in the periodic table, we find the uranium magnets, whereas in the d block, we find no f-derived magnets. For the uranium intermetallics, the position in energy of the d bands relative to those of the f bands seems to be crucial with regard to their magnetic properties [2], and this appears to be borne out by detailed band structure calculations [3]. d–f hybridization can delocalize the f. The sp electrons are less effective in this regard, it appears, although compounds such as UAl_3 are both not heavy and non-magnetic.

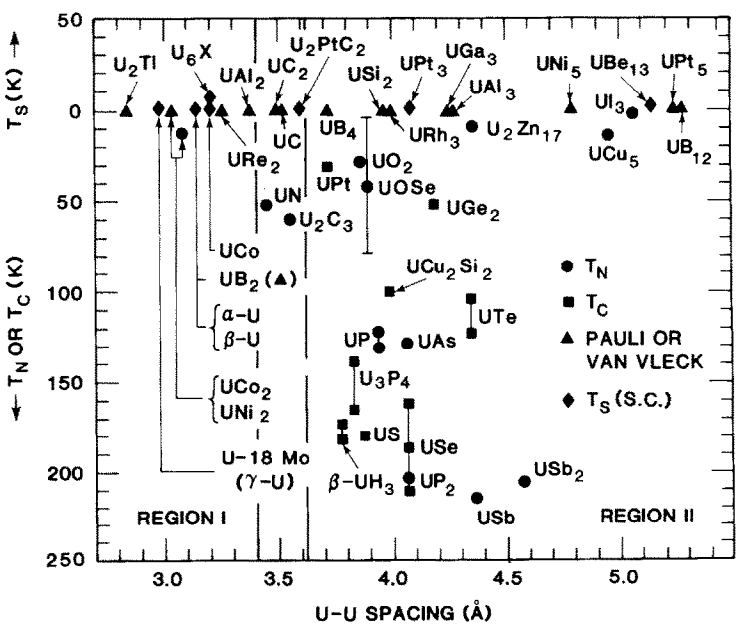

Fig. 2. Hill plot for U compounds.

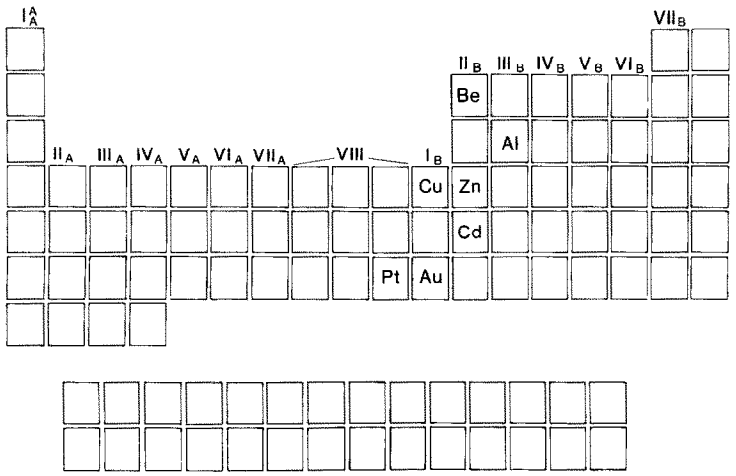

Fig. 3. Periodic table indicating with elemental symbols where the binary heavy electron compounds with U occur. Be and Mg have been moved from IIA to IIB.

				IIIB	IVB
				UAl_3 (Cu_3Au) — γ=41.6 mJ/mole K^2	USi_3 (Cu_3Au) — γ=14.0 mJ/mole K^2
				UGa_3 (Cu_3Au) T_N = 70K γ=52.0 mJ/mole K^2	UGe_3 (Cu_3Au) — γ=20.4 mJ/mole K^2
		IB	IIB		
URh_3 (Cu_3Au) —	UPd_3 (Ni_3Ti) $T_{str.}$= 7K, 5K γ = 5mJ/mole K^2	—	—	UIn_3 (Cu_3Au) T_N = 100K γ=49.9 mJ/mole K^2	USn_3 (Cu_3Au) γ = 169 mJ/mole K^2
UIr_3 (Cu_3Au) —	UPt_3 (Ni_3Sn) T_s = .5K γ = 450mJ/mole K^2	UAu_3 (UNKNOWN) T_N = 27K γ = 200mJ/mole K^2	UHg_3 (HEX) T_N = 50K(?)	UTl_3 (Cu_3Au) T_N = 90K	UPb_3 (Cu_3Au) T_N = 32K

Fig. 4. UX_3 compounds (structure given in parentheses); T_N, T_{str} and T_s are the Néel, structural and superconducting transition temperatures, respectively. Data compiled from ref. 5.

It is instructive to look at a series of uranium intermetallics at the 1:3 stoichiometry (Fig. 4). URh_3 and UIr_3 are both low γ metals for which experimental Fermi surface data as well as band structure calculations are available [4]. The next column contains the hexagonal compounds UPd_3 and UPt_3. UPd_3 has the double hexagonal stacking variant of the Cu_3Au

stacking: uranium has a local moment f^2 configuration here which undergoes quadrupolar ordering a 7 K, and a $\gamma(T = 0)$ value of roughly 5 mJ (mol U)$^{-1}$ K^{-2}. UPt_3, the simple hexagonal stacking variant, is a heavy electron superconductor with $\gamma = 450$ mJ (mol U)$^{-1}$ K^{-2}, $T_s = 0.5$ K. Column IB contains only UAu_3, of unknown structure. It appears to order perhaps antiferromagnetically at 27 K and have a $\gamma \approx 200$ mJ (mol U)$^{-1}$ K^{-2} at low temperature [6]. Column IIB contains UHg_3, with an unrefined hexagonal structure. We know from our own resistivity measurements that some kind of ordering occurs in this compound near 50 K. In columns IIIB and IVB we find that the higher Z members order antiferromagnetically with what appear to be good local moments.

In addition to this general trend towards local f-moment magnetism on moving from d elements to sp elements, with the heavy electron compounds caught between, there is also variation with local environment as well as relative concentration of the elements forming the compounds. For example, consider the sequence of U–Pt compounds (Fig. 5). UPt is a ferromagnet at 30 K, UPt_2 is non-magnetic and not heavy, UPt_3 is heavy as discussed above, and UPt_5 is non-magnetic with an enhanced $\gamma = 85$ mJ (mol U)$^{-1}$ K^{-2} [7]. An interesting aspect of UPt_5 is that substitution with Au to form $UAuPt_4$ increases γ to 725 mJ (mol U)$^{-1}$ K^{-2} (Fig. 6). There is some evidence that this is an atomically ordered compound, and that the gold atoms in this $AuBe_5$ lattice are situated so that uranium is tetrahedrally coordinated by them. It is interesting that this $AuBe_5$ structure is closely related to the cubic Laves phase of UAl_2. Half the uranium atoms in UAl_2 are replaced in an ordered way to form the $AuBe_5$ structure.

U Pt	$U Pt_2$	$U Pt_3$	$U Pt_5$
(CrB)	($Ni_2 Zn$)	($Ni_3 Sn$)	($Au Be_5$)
T_c = 30K	—	T_s = .5K γ = 450mJ/mole K^2	— γ = 85mJ/mole K^2

Fig. 5. Binary compounds of uranium and platinum. T_c is the ferromagnetic Curie temperature, T_s the superconducting transition temperature.

Drastic effects are also associated with certain types of impurity substitutions in heavy electron compounds. Nickel in UCu_5 [8] and copper in U_2Zn_{17} [9] at the few per cent level destroy the magnetic order. However, some column substitutions (silver for copper, cadmium for zinc respectively) have only modest effects on T_N. In UBe_{13}, 3 at.% Lu substitution for uranium roughly halves the γ of UBe_{13}; 3 at.% Th for uranium approximately doubles γ [10]. A tentative suggestion is that the electron per atom ratio is important, especially as regards the non-f bands in these materials, and this ratio could critically determine how uranium hybridizes with the conduction electrons.

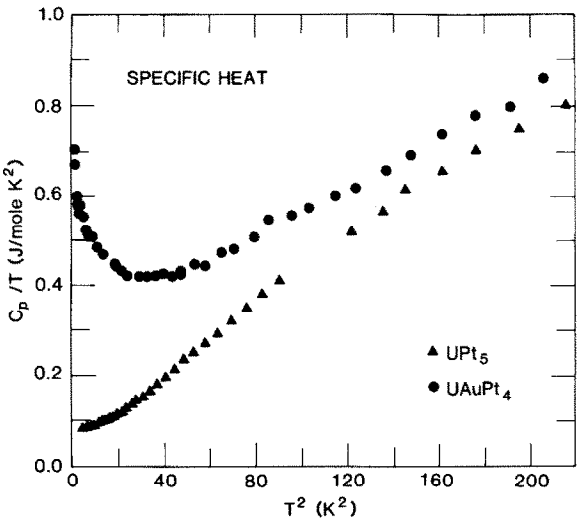

Fig. 6. Comparison of specific heats of UPt_5 and $UAuPt_4$. From unpublished data of H. R. Ott, H. Rudigier, E. Felder, Z. Fisk and J. D. Thompson.

3. Comments

If one thinks about the heavy electron compounds as having nearly localized f electrons, then it is somewhat strange that the really large γ materials of uranium and cerium are either superconductors or non-ordering, rather than of the heavy-electron magnetically ordering type. Another perspective on this comes from looking at the behavior of heavy electron compounds *vs.* the γ per unit volume, γ_V (see Table). There is a fairly regular progression from non-ordering through magnetically (but heavy) ordering to the superconducting ones (and the non-ordering $UAuPt_4$). This pattern encourages one to look for superconductivity in more perfectly ordered $UAuPt_4$. The recent report of a magnetic instability in thorium doped UPt_3 [11] is possibly an exception to this trend.

When the plot of γ *vs.* χ for compounds is examined (Fig. 1), we see that the superconductors lie closer to the free electron line drawn in the figure than do the magnetics. It is as if the superconductors have been more successful in converting their local moment entropy into conduction electron entropy. Experiments under hydrostatic pressure on UBe_{13} indicate that 6 kbar reduced γ by about 30% [12], while initial indications are that χ is unchanged within 10% at this pressure [13]. This suggests the unusual counter-intuitive idea that pressures of order 100 kbar might cause UBe_{13} to become magnetic, as its γ_V and χ values will now reside among those of the magnets.

Historically, Kondo-type effects, which seem to be related to much of the heavy electron physics, were first observed with transition metal impu-

TABLE 1

Electronic specific heats per mole uranium for various uranium compounds

Compound	γ (mJ mol^{-1} K^{-2})	γ_V (mJ cm^{-3} K^{-2})	*Ordering*[a]
α-U	12	0.96	s
UPt_5	85	1.38	n
URu_2Si_2	75	1.52	m, s
U_2PtC_2	75	1.59	s
UIr_2	52	1.63	n
URu_4B_4	170	1.63	n
U_6Fe	25	1.79	s
$U_2Co_3Si_5$	115	2.55	n
USn_3	169	2.84	n
UCu_5	210	4.03	m
UAl_2	150	4.25	n
U_2Zn_{17}	500	5.08	m
UCd_{11}	840	5.21	m
UPt_3	450	10.59	s
$UAuPt_4$	725	11.7	n
UBe_{13}	1180	13.55	s

[a]n, no ordering; m, magnetic ordering; s, superconducting.

rities in simple metals. No heavy electron compounds of transition elements with non-f elements have been identified as yet, but one suspects that they must be there. The problem is that, most probably, the transition metal case is more complicated: in heavy electron f compounds we are only concerned with spin fluctuation effects. In transition metal compounds, the electrons involved in developing magnetism are also involved in bonding. This means that charge fluctuations will be equally important. The heavy electron f compounds, therefore, are a kind of projection of one part of the more complicated transition metal problem. The hope is that we will be able effectively to apply to the transition metals the insights obtained from the heavy electron f compounds.

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