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f-electron hybridization and heavy-fermion compounds

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Hybridization between *f* orbitals and non-*f* ligands on neighboring sites is discussed as the primary mechanism determining the bandwidth and properties of certain Ce and U compounds, including the heavy-fermion metals. The occurrence and systematic variation of heavy-fermion and related behavior in the Periodic Table is interpreted in terms of this hybridization mechanism, with a specific discussion of experimental data for the UX_3 compounds. Several experiments are suggested to clarify and extend these ideas.

I. INTRODUCTION

The heavy-fermion compounds of Ce and U are characterized by very large electronic specific heats corresponding to electronic effective masses as much as several hundred times the free-electron mass. The magnetic properties of these materials are typical of narrow-band metals, ranging from enhanced Pauli paramagnetism through spin fluctuation and Kondo-lattice behavior, to itinerant magnetism. In some cases superconductivity associated with the heavy electrons has been observed, and the possibility of *p*-wave pairing has been discussed. Because so few heavy-fermion metals are known, there has been no attempt to understand the occurrence and systematics of their behavior within the Periodic Table. In this paper we develop such systematics, concentrating on the role of hybridization of the *f* electron with *s*, *p*, and *d* orbitals on neighboring non-*f* atom sites (referred to hereafter as *f*-ligand hybridization). We emphasize that the Hill model of localization of *f* electrons by large *f*-atom separation is *not* the primary mechanism responsible for heavy-fermion behavior in the known systems. In cases where the *f*-atom separation is large, we show that the strength of the *f*-ligand hybridization controls the itinerant electron bandwidth, producing "wide-band" transition metal-like behavior (e.g., UGe_3, UIr_3, URh_3), narrow band behavior (USn_3) and local-moment behavior (UPd_3, UPb_3, UTl_3). Where the *f*-ligand hybridization is strong enough, it has been well-characterized theoretically through band-structure calculations and experimentally through Fermi surface experiments. In cases where the *f*-atom separation is small, we suggest that *f*-ligand hybridization may still be important or even dominant. Using simple arguments concerning the overlap of *f* orbitals with ligands on neighboring sites we infer qualitative rules concerning the strength of the hybridization. Finally, we correlate trends in *f*-ligand hybridization within the Periodic Table with the occurrence of heavy-fermion behavior and suggest experiments to test and extend our ideas. In this discussion we concentrate on the UX_3 compounds, most of which have the $AuCu_3$ structure, and which span all the relevant metallic behaviors including Pauli paramagnetism, mixed valence, spin fluctuation, heavy-fermion and local-moment magnetism.

There are two aspects of heavy fermion systems that we do not discuss. (1) Although a high density of states from one-electron hybridization is a requisite driving force for heavy-fermion behavior, it is not the only mechanism contributing to the observed properties. The large specific heats of the heavy-fermion metals probably cannot be achieved without considerable many-body enhancements. In this regard, the heavy-electron metals differ from the majority of *f*-electron compounds with lower electronic specific heats which usually exhibit only small or moderate enhancements. (2) A large density of states at the Fermi energy is often unstable. Jahn-Teller—like arguments show that it is often favorable for the system to undergo a phase transition in order to lower the energies of the occupied states. This change of phase can take many forms—a crystallographic change, magnetic ordering, the occurrence of charge or spin density waves, or superconductivity. It is remarkable that several of the heavy-fermion systems do not undergo such a transition. Although these two additional aspects are both significant and interesting, we do not discuss them here. The emphasis in this paper is on the fundamental hybridization processes which delocalize the *f*-electron and lead to narrow-band behavior at the Fermi energy.

II. DELOCALIZATION BY DIRECT *f*-*f* HYBRIDIZATION

Qualitative consideration of direct *f*-*f* interactions is relatively easy because the controlling parameter is the interactinide separation, independent of crystal structure in the first approximation. Because the spatial extent of the *f* orbital is just slightly larger than the highest *p*-core orbital, the actinides must be reasonably close together for pure-*f* bands to form, but once the overlap criterion has been satisfied, the *f*-orbitals will delocalize. Hill classified these materials[1] by identifying local-moment magnetism as a signature of localization, and superconductivity or Pauli paramagnetism as a signature of itinerancy. Plotting the magnetic and superconducting transition temperatures as a function of the interactinide separation, he found a reasonably sharp transition with the "localized" compounds above a critical atomic separation region and the "itinerant" compounds below that region. The natural interpretation of this observation is that the *f* band has become very wide for small interactinide separations and very narrow (or no longer a band) for large interactinide spacings. Compounds such as U_6Fe, $CeRu_2$, and $CeCo_2$ have small separations by the above criteria and have often been described as having wide bands due to direct *f*-*f* overlap. However, as we discuss in the next section, hybridization with non-*f* orbitals must also be considered.

III. DELOCALIZATION BY *f*-LIGAND HYBRIDIZATION

Although the success of the Hill plot shows that direct *f*-*f* overlap determines the degree of itinerancy in many compounds, it is clear that this alone will not explain all of the observed phenomena. There are notable exceptions to the Hill correlation where the *f*-atom separation is large yet no magnetic order is observed. In particular, UIr_3,[2] URh_3,[2-4] and UGe_3 (Refs. 5-7) behave remarkably like transition metals, with "low" specific heats, temperature-independent Pauli susceptibilities, and ordinary resistivities. In these materials, extensive Fermi-surface measurements[8-11] combined with band-structure calculations[10-13] show explicitly that the *f* electrons are delocalized by hybridization with the *s*, *p*, and *d* states on neighboring nonactinide atoms. In the case of UGe_3, a specific examination was made of the possibility that the predominant *f*-delocalization mechanism is an interaction between a U *f* orbital and a *d* orbital on a neighboring U atom.[11] This seems like a reasonable possibility since the U atoms sit on a simple-cubic structure with no intervening Ge atoms, but it was found not to occur. These materials provide the most convincing and well-documented evidence for the importance of *f*-ligand hybridization in the large separation limit. The hybridization is so strong that all vestiges of narrow *f*-band behavior have disappeared.

Other exceptions to the Hill criteria can also be found. $NpAl_2$ has a relatively large *f*-atom separation and was thought to have local behavior, but is now known to have itinerant *f* electrons.[14] The heavy-fermion materials themselves all have large *f*-atom separations, yet their high electronic specific heats show that the *f* electrons are mixed with itinerant states. Among Ce compounds the exceptions to the Hill criteria have been intensively studied within the context of the mixed-valence problem.[15] These materials typically show many narrow-band effects indicative of *f*-electron delocalization. Evidence for *f*-ligand hybridization can be found in band calculations for the Ce cubic Laves phases,[16] and in the combined band-structure and Fermi-surface experimental studies of $CeSn_3$.[17,18] Although band calculations and de Haas—van Alpen experiments are difficult in $CeSn_3$ because the band widths are narrow, the many-body effects strong, and the effective masses large, these studies confirm that *f*-ligand hybridization is the primary mechanism of *f* electron delocalization.

f-ligand hybridization operates equally well for large and small *f*-atom separations. At high separations there can be no direct *f*-*f* overlap, so that *f*-ligand hybridization accounts for the delocalization of the *f* electrons. However, at low separations, both direct *f*-*f* overlap and *f*-ligand hybridization may delocalize the *f* electrons. Remarkably, band-structure calculations of Ce Laves phase compounds ($CeCo_2$, $CeRu_2$, $CeOs_2$, etc.) whose *f*-atom separations are below or near the critical Hill limit, show little direct *f*-*f* interaction but considerable *f*-ligand interaction.[16] Thus even for small *f*-atom separations, *f*-ligand hybridization may be the dominant mechanism of *f*-electron delocalization. In this regard the U_6X (X = Fe, Co, Ni) compounds[19] are of interest. In many ways, their superconducting properties are similar to those of the heavy-fermion superconductors UPt_3,[20] UBe_{13},[21] and $CeCu_2Si_2$,[22,23] and the systematics of their normal-state properties follow the pattern discussed below for *f*-ligand hybridization. Thus, it is at present an interesting but unresolved question whether the *f*-electron delocalization in these compounds occurs by direct *f*-*f* overlap, making it different from the other heavy-fermion superconductors, or by *f*-ligand overlap, in which case it is in the same class as UPt_3, UBe_{13}, and $CeCu_2Si_2$, but with a wider bandwidth.

In what follows we examine the *f*-ligand hybridization more closely. Specifically, we propose that the strength of the *f*-ligand hybridization determines the bandwidth and the anomalous properties of 4*f* and 5*f* compounds, which are exceptions to the Hill criterion. As we show below, the strength of the *f*-ligand hybridization depends sensitively on the crystal structure and the properties of the non-*f* atoms, so that one can find, and perhaps create, materials with any desired amount of narrow band character.

IV. STRENGTH OF THE *f*-LIGAND HYBRIDIZATION

We will now consider some qualitative features of the coupling between the *f* orbital and the remaining orbitals of the system. For simplicity, we assume a local interaction, and consider the overlap of the orbitals as a measure of the hybridization. Because of the short range of the *f* orbitals, a qualitative analysis can be obtained by performing a Taylor series expansion of the non-*f* orbital from a neighboring site about the position of the *f*-orbital atom.[24] If ϕ is an *s*, *p*, or *d* orbital on a non-*f* atom and $\mathbf{R}_f$ the position of the *f* atom, then

$$\phi(\mathbf{R}_f+\mathbf{r})=\phi(\mathbf{R}_f)+\sum_i \left[\frac{\partial\phi}{\partial r_i}\right]_{R_f} r_i+\frac{1}{2}\sum_{ij}\left[\frac{\partial^2\phi}{\partial r_i\,\partial r_j}\right]_{R_f} r_i r_j + \frac{1}{6}\sum_{ijk}\left[\frac{\partial^3\phi}{\partial r_i\,\partial r_j\,\partial r_k}\right]_{R_f} r_i r_j r_k+\cdots \qquad (1)$$

Expressing the radial factors as sums of spherical harmonics and using the orthogonality properties of spherical harmonics, one can easily show that the constant, linear, and quadratic terms in Eq. (1) are orthogonal to an *f* orbital (represented by the Y_3^m spherical harmonics) centered at $\mathbf{R}_f$. Thus, only cubic and higher-order terms of the non-*f* wave function contribute to the overlap integral. Consequently, it is the spatial variation of the non-*f* orbital, rather than its magnitude, which will determine the strength of the *f*-ligand interaction. At the position of the f atom, the derivatives are small and drop off rapidly with increasing order. Furthermore, the overlap integral will involve a large power of the radius, because only the high-order terms in the expansion appear, and so will emphasize large radii relative to the position of the f atom. In this region the amplitude of the f wave function is small. One therefore sees that the matrix elements between an f orbital and a non-f orbital from a neighboring site are generally small.

This analysis suggests several features of the f-ligand interaction which are pertinent to the formation of hybridized f bands.

(1) The controlling feature of the f orbital is the size of the tail at large r, since only high-order terms in the Taylor series expansion contribute. This selects light rare earths and actinides, where the f orbitals have small but slowly decaying tails, but is relatively insensitive to the choice of the particular element. Because of the lanthanide (or actinide) contraction, the f orbitals in the heavy rare earths or actinides, are less extended in space, and are not so strongly affected by hybridization.

(2) Because the spatial variation of the non-f orbital controls the size of the matrix element, that atom will be primary in determining the behavior. As a result, there is a great deal of parallelism between isostructural Ce and U compounds which have the same non-f elements. Thus, $CeSn_3$ is a mixed-valence system which has substantial f involvement in the conduction bands,[17,18] as does USn_3 with its large electronic specific-heat coefficient[6] of 169 mJ/mole K^2. Similarly, $CeRh_3$ (Ref. 25) and URh_3 (Refs. 8–10) both show itinerant f-electron behavior. These parallels are numerous and appear to work generally except in cases where the crystal structures are different.

(3) f-orbital hybridization will be most favorable at the top of the non-f orbital bands. This arises because the structure of the non-f orbital is more significant than its magnitude, and the orbital has a higher kinetic energy (and hence more curvature) at the top of the band. This effect is seen[26] in the dioxides of Ce, Pr, and the actinides, where f character is only admixed at the top of the oxygen $2p$ band. The same will be true for UC, as well as the pnictides, chalcogenides, dialuminides and $AuCu_3$ compounds of Ce and U.

(4) Since the individual matrix elements contributing to the hybridization are small, the most pronounced effects will occur in cases where the near-neighbor coordination with non-f atoms is large. The importance of high coordination is seen in UBe_{13} and UPt_3, which have coordination numbers of 24 and 12, respectively.[27,28]

(5) When comparing materials of different structures, effects related to the angular dependence of the orbitals must be considered because the specific nature of the hybridization depends on the geometric placement of the atoms involved. A particularly striking example is the comparison of UPt_3, which is a heavy-fermion superconductor having the $MgCd_3$ structure, with the isoelectronic compound UPd_3, which has the $TiNi_3$ structure and is a local-moment system.

V. SYSTEMATICS OF f-LIGAND HYBRIDIZATION

The qualitative discussion of f-ligand hybridization given above suggests that there are systematic trends in the bandwidths and properties of Ce and U compounds as the non-f atom varies throughout the Periodic Table. In the following we will demonstrate such systematics for the UX_3 compounds, where a large amount of data is available. Some basic information characterizing the electronic and magnetic properties of these materials is given in Fig. 1, and structural data is given in Table I. With the exceptions of UPd_3 and UPt_3, these compounds all have the $AuCu_3$ structure, so that variations in the bandwidths and properties of these materials are due to changes in the non-f-atom orbitals and lattice constants.

TABLE I. Structural data for UX_3 compounds [see A. E. Dwight, in *Developments in the Structural Chemistry of Alloy Phases*, edited by B. C. Giessen (Plenum, New York, 1969), pp. 181–226].

Compound	Structure type	Lattice constant (Å)	U—X distance (Å)	U—U distance (Å)
USi_3	$AuCu_3$	4.035	2.853	4.035
UGe_3	$AuCu_3$	4.206	2.974	4.206
UGa_3	$AuCu_3$	4.248	3.003	4.248
UAl_3	$AuCu_3$	4.287	3.031	4.287
UIn_3	$AuCu_3$	4.601	3.253	4.601
USn_3	$AuCu_3$	4.626	3.271	4.626
UTl_3	$AuCu_3$	4.674	3.306	4.674
UPb_3	$AuCu_3$	4.792	3.388	4.792
URu_3	$AuCu_3$	3.977	2.812	3.977
URh_3	$AuCu_3$	3.991	2.822	3.991
UIr_3	$AuCu_3$	4.023	2.845	4.023
UPd_3	$TiNi_3$	$a = 5.757$ $c = 9.621$	2.878–2.923	4.102
UPt_3	$MgCd_3$	$a = 5.764$ $c = 4.898$	2.876–2.955	4.123

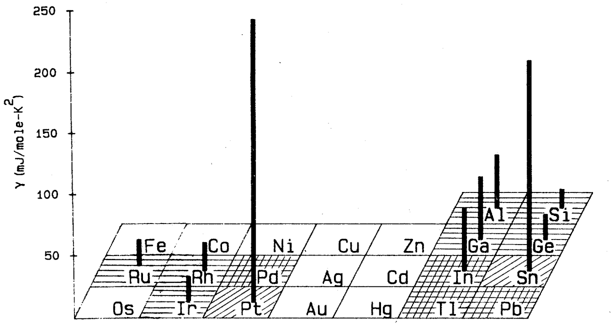

FIG. 1. Rough overview of the electronic and magnetic properties of UX_3 compounds, where X is indicated in the figure. Vertical bars show the value of the electronic specific-heat coefficient, γ. Horizontal hatching indicates Pauli paramagnetism. Diagonal hatching indicates spin-fluctuation behavior. Crosshatching indicates local-moment behavior. Data is taken from Refs. 2—7, 20, 29—36. An extensive review of the data has been given by J. Fournier and R. Troc, in *Handbook on the Physics and Chemistry of the Actinides,* edited by A. J. Freeman and G. H. Lander (North-Holland, Amsterdam, in press). Superconductivity is observed at 0.2 K in URu_3 (Ref. 31) and 0.54 K in UPt_3 (Ref. 20).

In the following, we will show that systematic behavior can be seen if we assume that the f-ligand hybridization decreases as the size of the X atom increases, i.e., as one moves down a column in the Periodic Table. This is consistent with the increasing U-X distance (Table I) and with a proposed competition between f-p and p-p hybridization.[11] For small X atoms (strong hybridization) one then expects Pauli paramagnetism with a relatively low density of states at the Fermi surface, although it may be larger than for transition metals because of the f electron involvement. For large X atoms, one expects local-moment behavior with a low density of states at the Fermi surface. For intermediate hybridization, a large density of states should be observed, depending on the degree of hybridization and the position of the local f-electron energy relative to the Fermi energy. In this region, one should see heavy-fermion behavior and possibly spin-fluctuation effects.

This trend is clearly seen in Fig. 1 when X is taken from the group-IV elements Si, Ge, Sn, and Pb, with lattice constants increasing monotonically from 4.035 Å for USi_3 to 4.792 Å for UPb_3. Both USi_3 (Refs. 5,6,36) and UGe_3 (Refs. 5—7,30) show temperature-independent paramagnetism over a wide temperature region, with γ values of about 40 mJ/mole K^2, corresponding to strong hybridization. USn_3 has a γ value of 169 mJ/mole K^2, and so is in the transition region.[5,6,30] The transition to local-moment behavior is complete with UPb_3, which has an antiferromagnetic transition at 32 K.[32,33] It is interesting to speculate whether the maximum density of states has been reached at USn_3, or whether minor changes in stoichiometry around that compound could increase it substantially. The correspondence between Ce and U compounds with the same non-f elements suggests that the large electronic specific heat in USn_3 is due to strong many-body effects as well as one-electron hybridization, since both effects are important in $CeSn_3$.[17,37,38]

Direct evidence for the f-ligand hybridization in UGe_3 comes from Fermi-surface data.[11] Further evidence can be obtained from neutron measurements of the magnetization density induced in UGe_3 and USn_3 by an external magnetic field.[39,40] A striking feature in UGe_3 is the occurrence of a pronounced magnetization density very close to, but not centered on, the Ge site.[39] This can be interpreted within an f-p hybridization model if we note that the response of the system to a magnetic field is dominated by the response of the f orbitals. In the simplest treatment, the energy of an f-p hybrid is assumed to be Zeeman split according to the action of the field on the f-orbital part. The Ge p orbitals that are admixed with the two spin states of the U atom thus have slightly different energies and slightly different radial wave functions. This difference, proportional to the derivative of the Ge wave function with respect to energy, can be examined by band structure calculation, and is found to have its maximum precisely where the magnetization density is observed (on the leading edge of the Ge $3p$ principal lobe). This effect is not seen[40] in USn_3 in spite of a much larger susceptibility, but consistent with weaker f-p hybridization. It would be desirable to have such data for USi_3, where the hybridization should be stronger and the anomalous magnetization near the Si site larger, but sufficiently large single crystals of this material are not available.

We next consider compounds with X taken from the group-III elements Al, Ga, In, and Tl. Since group-III elements will give a Fermi energy lower in the p bands than group-IV elements, one expects to find a reduced f-ligand hybridization, and a stronger competing p-p interaction. Consequently, one expects narrower f bands, a higher electronic specific heat and a transition to local behavior at smaller values of the lattice constant than for the group-IV series. Thus, UAl_3 and UGa_3 show[5,6,34] temperature-independent paramagnetism with γ values of approximately 50 mJ/mole K^2. Both UIn_3 and UTl_3 show[5,6,34] well-defined Curie-Weiss behavior in the susceptibility, with a maximum at approximately 90 K. This has been attributed both to crystal field effects[34] and to the occurrence of a magnetic ordering,[35] either explanation implying the presence of localized f electrons. We may thus anticipate heavy-fermion-type behavior for compounds with electronic structure intermediate to UGa_3 and UIn_3, where the transition from itinerant to local electrons seems to occur. The region between UIn_3 and USn_3 is also of interest since the two endpoints have almost the same lattice constant, but span a transition from spin fluctuation to local-moment behavior.

Finally, we consider the compounds formed with the d-transition elements, $X =$ Ru, Rh, Ir, Pd, and Pt. URh_3, URu_3, and UIr_3 are normal itinerant materials with fairly small electronic specific heats. More is known about URh_3 and UIr_3 than URu_3, which has just been found to be a superconductor.[31] Because of charge transfer, the transition-metal d band is just filled in these materials, and the d band character at the Fermi energy is due to d-f hybridization. This is strong enough that these materials behave in a simple fashion. For example, photoemission data can be interpreted in a standard band picture with very small relaxation shifts.[41] de Haas—van Alphen measurements can be compared with band calculations with excellent success, and show very small mass enhancements.[8,9,12,13]

In the case of UPd_3 and UPt_3, with one more d electron than URh_3 or UIr_3, one expects the d band to be pulled further below the Fermi energy, thus weakening the f-d hybridization. This is consistent both with the observation of local moment behavior in UPd_3 and of heavy-fermion behavior in UPt_3. However, the comparison is substantially complicated by the fact that neither of these compounds exist in the $AuCu_3$ structure, the structure change corresponding to fcc→dhcp for UPd_3 and fcc →hcp for UPt_3. If the trends of the group-III and group-IV elements were maintained here, one would expect to see the heavy-fermion effects in UPd_3 and local moments in UPt_3. This discrepancy with the observed behavior emphasizes the importance of the crystal structure in determining the degree of f-ligand hybridization. It is interesting to note that $CePd_3$, which does form the $AuCu_3$ structure, is mixed valent rather than magnetic.[15] The importance of structure is also visible in $NpPd_3$, which can be stabilized in both structures. The cubic compound shows magnetic behavior with an antiferromagnetic transition at 55 K, while the hexagonal compound shows ambiguous and poorly understood magnetic effects with no apparent long-range ordering.[42] It would be very interesting to attempt to stabilize UPd_3 in the $AuCu_3$ structure.

VI. CONCLUSIONS

A general discussion has been given which clarifies the nature of the hybridization of f electrons with non-f electrons, and its role in determining the electronic properties of the light actinides and Ce compounds. In particular, attention has been addressed to the occurrence of heavy-fermion compounds, and the way in which that behavior is related to more common phenomena such as mixed valence and spin fluctuations. These ideas were used to discuss the observed electronic and magnetic properties of the UX_3 compounds. In order to explore these ideas further, we suggest the investigation of a number of pseudobinary systems. Compounds of the form $USn_{3-x}Pb_x$ and $USn_{3-x}Ge_x$ completely cover the range of behavior from itinerant electrons, through spin fluctuation with large effective masses, to local-moment behavior. Similarly, the system $USn_{3-x}In_x$ allows a transition from local-moment to spin-fluctuation behavior, with the added advantage of maintaining the lattice constant approximately unchanged. The compounds $UPt_{3-x}Ir_x$ and $UPt_{3-x}Pd_x$ also allow one to consider the change from a heavy-fermion system to either itinerant electrons or local moments, with the additional factor that the crystal structures are different, thus allowing an assessment of the importance of structure in determining the properties. Finally, it would be very interesting to attempt to stabilize both UPd_3 and UPt_3 in the $AuCu_3$ structure. A number of these experiments are currently underway.[43,44]

ACKNOWLEDGMENTS

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