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THE BAND DESCRIPTION OF MATERIALS WITH LOCALIZING ORBITALS*

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ABSTRACT

Density functional theory is a form of many body theory which maps the problem onto an equivalent single particle-like system by limiting to the ground state (or some limited ensemble). So it should be surprising that this ground state theory could have any relevance whatsoever to the excitation properties of a material--and yet it does when used carefully! However, the most interesting materials involve active orbitals which are at least partially localized in space and this has profound effects both on the ground state and the excitation spectrum. My long term interest is in Ce and actinide compounds such that the popular concerns are mixed valence, heavy fermions, and the various forms of magnetic transitions. Band structure calculations can give a great deal of information concerning the mechanisms and degree of the localization as will be shown by examples using the Ce and U Ll_2 structured materials and the Ce cubic Laves phase materials. There are some difficulties due to an incomplete knowledge of the functionals involved which causes an underestimate of the local character. This will be illustrated and discussed.

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INTRODUCTION

The first section of this paper was strongly motivated by the claim that the two f-peak structure observed for Ce materials was a major failure of band theory. The corollary then applied was that band theory could have no applicability to Ce materials at all. This perception persists in spite of considerable work demonstrating a reasonable description of the energetics. The crux of the matter lies in the localization of the f-orbitals and the resultant "correlation" effects. So we again come back to the discussion of localization that has permeated actinide and rare earth research. Admittedly, f-orbitals are not the only systems to demonstrate such phenomena but they are definitely members of the class with a certain simplicity. One interesting result to appear recently is the fact that hybridization can dominate as the broadening mechanism even when direct f-f interactions are possible. This is exhibited very clearly in the Ce cubic Laves phase compounds. But the systems for studying hybridization effects are the Cu_3Au structured materials. These will be used to discuss some systematic behavior germane to the discussion of heavy fermion behavior. One proviso is in order. This exposition is highly personal and provential. The purpose is not to imply that there is not a lot of work being done in the field but to advance my own views within the time and space limitations. I am comfortable in doing this as most other workers in the field are present and can represent their work better than I.

BAND THEORY AND EXCITATION PROPERTIES

Band theory is an unusual exercise in that it can be based on one of several underlying formalisms [1]. The most common formalism in current use is based on density functional theory (DFT) [2] with the mapping onto the effective single particle system following Kohn and Sham [3]. Although there

are generalizations of this formalism to deal with limited ensembles [4,5], general use is normally based on the ground state formulation--an aspect that DFT shares with most other formulations that could be used to derive a band theory. Clearly, the band theory is an optimized formalism for the ground state. Thus one should use it to discuss cohesive energies, lattice constants, phase stabilities, and bulk moduli. One is admonished that the "single particle eigenvalues" have no physical significance and indeed their values can change considerably as one chooses different implementations. Yet, we persist in utilizing band structures to discuss specific heats, Fermi surfaces, optical data, photoemission, and any other excitation property that one might imagine.

To extend a density functional formalism to a single excited state, it would be necessary to maintain orthogonality to the ground state system throughout the variation used in the derivation. This is not clearly achievable except in the special case of having a definitive change in symmetry. However, if one makes the leap of faith that one always has such a symmetry change, then the original Hohenberg-Kohn development could be carried through for excited states. (This is not really correct [6].) Consequently, although one does not have a strong formal underpinning for the application of a DFT-like approach to excited states, one can argue that it is not an unreasonable beginning. There is the second "engineering detail" that arises from our almost inadequate knowledge of the requisite functionals. One should note, however, that the local density approximation (LDA) used extensively for the ground state should not work there for most interesting systems. Yet it does do amazingly well. Given such a state of affairs for the ground state, why not use it for the excited states as well? This forms a very tenuous basis for a procedure which has actually worked quite well.

Why? Again the answer is questionable but I would assert the following. Two things this approach deal with in a reasonable fashion are the variations in the kinetic energy and the direct Coulomb energy. These are the major energy terms that are focussed on by the the model Hamiltonians such as the Anderson and Hubbard models. The screening effects of the exchange-correlation functional are much smaller so the larger percentage error is more tolerable.

Some observations are in order concerning the relationship between a DFT treatment of the f-electron system and the more analytic schemes based on an Anderson or Hubbard Hamiltonian. It is true that one must strain to extend density functional theory to the excited states. But this should be balanced by the fact that the model Hamiltonians are gross simplifications that one hopes will capture the essence of the problem. An instance where one must worry about the nature of such a translation occurs below in the discussion of the makeup of the poorly screened peak. It will be of considerable interest to ask how one defines the parameters of the model Hamiltonian which in the end may teach us more than the knowledge of its solutions.

With the arguments that the use of a DFT should be acceptable for excited state properties, let us take it as a postulate and proceed to examine its application. In spite of the fact that the Kohn-Sham treatment maps the problem onto a set of effective single particle states, DFT is still a many body theory. As such, the excitation energy of the system must be determined as a total energy difference. This difference can often be determined using a Slater transition state [7] analysis. Janak has provided the basis for extending this to DFT by showing the eigenvalue to be the occupation number derivative of an analytic continuation of the total energy

$$e_v = dE_{TOT}/dn_v \quad (1)$$

The total energy expression is formally only valid at integer occupation numbers and a "true" total energy expression for non-integral occupation numbers would need to be an ensemble average. This is an important question that we avoid by working with an analytic continuation--and recognizing it as such. The total energy change in transferring an electron from the state μ to the state ν is thus

$$\Delta E_{TOT} = \int_0^1 [e_\nu(\eta) - e_\mu(1-\eta)] d\eta \quad (2)$$

Given that the eigenvalue dependence on η is very nearly linear,

$$\Delta E_{TOT} = e_\nu\left(\frac{1}{2}\right) - e_\mu\left(\frac{1}{2}\right) \quad (3)$$

which is the standard application of transition state arguments. But, one could almost as well use

$$\Delta E_{TOT} = \frac{1}{2} \{ [e_\nu(0) - e_\mu(1)] + [e_\nu(1) - e_\mu(0)] \} \quad (4)$$

which is the average of the the eigenvalue difference in the ground and the excited state. The band structure results give only half of this expression. It follows that the band structure results will fail to represent the excitation energy whenever the excited state eigenvalues differ from the ground state eigenvalues. The usual argument in standard elementary solid state texts is that this will not happen because of the itineracy of the states. The band states are spread across the N unit cells of the crystal so

the change in density in a single unit cell is proportional to $1/N$ and should be negligible. Where this is true, the band energies form an adequate representation of the excitation spectrum. However, the situation changes if the excitation is more localized. A clear case arises when a deep core electron is ejected in a photoemission process. The final state then looks to the conduction electrons like a $(Z+1)^+$ impurity if the hole is not screened. In actuality, much of the interesting physics comes from the competing screening processes and their materials systematics [9]. This particular example is mentioned as it has strongly influenced our efforts with the f-state photoemission process in Ce compounds [10]. Although the f-states are not deep, they can be locally excited.

The incomplete atomic shells of Ce are the 4f, 5d, and 6s with an atomic ground state of $4f\ 5d\ 6s^2$. Because the principal quantum number is a major factor governing the radial extent of an orbital, the 4f is much more compact than the 5d, and the 6s is quite extended. The principal maximum of the 4f actually lies at or just inside that of the 5p core states. The standard rare earth-like treatment for Ce would then view the 4f states as atomic-like levels in a crystal field environment. But the tale is in the tail. Because the 4f lies much higher in energy than the 5p, it has a small but much more extended tail [11] which opens the possibility of hybridization with orbitals from neighboring atoms. Many Ce materials have hybridized f-states in the ground state, as will be discussed further below. If this broadens the f-levels out into bands, it is extremely likely that they will occur at the Fermi energy as only one f-orbital is occupied out of a possible 14. (One can find exceptional cases where this would not be the case, of course.) If the excitation is delocalized, this would result in spectral density at the Fermi energy. Incidentally, this would also be true if the excitation were so

sudden that the exiting electron escaped before the system could relax--but we discount this possibility. The hybridization is weak, however, and easily broken by the energetic photon so it is possible to create an excitation similar to a local atomic excitation. If such a hole were not screened by the surrounding conduction electrons, the system would be left in a strongly excited state. But such a screening does take place in most cases and can be viewed in an LCAO picture as a repopulation of quasiatomic orbitals. The best such screening would occur through the repopulation of f-orbitals which have the same radial extent as the excited orbital. The jargon for this case is the "fully screened case." Because of its similarity to the ground state, one can appreciate that it will be a very low lying excitation and we will neglect that excitation energy. This is a third scenario by which the excitation energy will be given by the ground state band structure. Obviously, it is easy to find a mechanism for the appearance of a peak at the Fermi energy from the band approach (in contradistinction to the Anderson model approach which creates it as a Kondo resonance peak). It is not as clear as to the exact mechanism although I am strongly biased to the fully screened interpretation for the rare earths. A new feature appears if the fully screened channel is blocked or at least throttled. In that case, the screening may be accomplished by occupation of the d orbitals which are of greater radial extent and thus cannot screen as well. This must be a higher energy excited state and thus the photoelectron will exit with a lower energy--just as though the initial state energy had been lower. This is the "poorly screened peak." The energy shift of this peak is roughly an $f \rightarrow d$ transition energy. In Ce compounds, this peak appears 2-3 eV lower in energy than the fully screened peak because the system is left in an excited state. This is the second peak that does not appear in the ground state density of states--

because it should not! It should be clear at this point that it is not appropriate to dismiss a band structure approach because this peak is not in the density of states.

To illustrate that this picture has an element of truth, we have performed a series of calculations [10] demonstrating that it does properly reproduce the energetics of the problem. The systems chosen were the Ce pnictides because (a) one can examine the systematics of these isostructural, isoelectronic materials and (b) their rock salt structure is sufficiently tractable that one can afford to lower the symmetry to deal with the excited state. The approach involves first doing the ground state calculation to gain information about the f-peak near the Fermi energy as well as the pnictide p-bands. An impurity technique--the supercell--is utilized to gain information about the second peak. In this scheme, one examines an expanded unit cell where one atom is treated as an excited (impurity) atom. The model is actually an array of excited atoms but, if the excitation is sufficiently local that their coupling is negligible, it can approximate the isolated impurity. For Ce, one can introduce the excited state by omitting the capability to describe the 4f on the site. In the case of the linearized augmented plane wave (LAPW) method used, this is accomplished by setting the controlling energy parameter into the range of the 5f's. A self-consistent calculation is then carried out for the system thus constrained. Once the potential is determined in this manner, the 4f states are located to provide the excited state eigenvalue to apply in Eq. 4. (Note that this approach has assumed a metal in contact with an electron reservoir to provide the screening electrons.) Excellent results are obtained differing from experiment by one or two tenths of an electronvolt and the larger errors can actually be traced to the prescription applied actually removing too much f-charge. The excited

state can also be examined to determine the nature of the screening charge. It is found to be nearly all Ce d-orbital in nature--the pnictide p's being further removed. This result has the interesting implication that the interpretation of the Anderson model studies must be that the model must be formulated using f-d hybrid quasiparticles which are then coupled to the remaining more itinerant electrons.

The appearance of this second poorly screened peak depends on the metastability of the screened hole. If it is not sufficiently localized, it will quickly decay and not be detectable. Note the case of CeN [10]. It is the nature of the excited state that is important. This can be seen from materials systematics as well as from the above discussion. One can assert that the occupied f-states in U have roughly the same degree of localization as those in Ce when in the ground state. Yet the poorly screened peak has not been seen in the photoemission of U. To support the assertion of comparable ground state localization, consider the following. CeSn_3 is a mixed valent system while USn_3 is nearly a heavy fermion material (which becomes so when about a third of the Sn is replaced by In). CePb_3 is a weak antiferromagnet which is a heavy fermion system with small additions of Sn (or at a slightly raised temperature or with an applied field). UPb_3 is an antiferromagnet. CePd_3 is a mixed valent material. (CePd_3 does pass through a heavy fermion regime into a localized magnetic system with the addition of B.) UPd_3 has undergone a phase transition away from the Cu_3Au and exhibits crystal field behavior. These last two examples would actually suggest that it was U that exhibits the more localized behavior. But the evidence indicates that ground state f-localization is not all that different in the Ce and U materials. What is different is the change in going to the excited state. Ce goes from one f-electron down to zero whereas U is merely decreasing 2-3 f-charges by

one. This is certainly not proof but is highly suggestive that there should be a qualitative difference between the two. In most cases, the much smaller value of the intra-atomic Coulomb integral found for U will also play a role. Nonetheless, it would be most interesting to perform some studies for uranium. There is, however, the small detail that thus far we have been excluding f-charge in the case of Ce. The problem for U can be handled by treating the f-orbitals as core like where one inputs the occupation number as input--not a desirable procedure for U--or by introducing a variational constraint [12].

Photoemission involves a very strongly interacting probe and it is easy to imagine that the probe could dramatically affect the system. Let us turn to a much gentler situation--the electronic specific heat. To establish a proper theoretical description, one should utilize the thermal statistical ensemble formulation of density functional theory. However, useful insight can be gained from the more developed ground state formulation coupled with the Sommerfeld expansion. Doing so neglects partially known corrections [13] but is the standard approach in metals and works reasonably well when the electron-phonon coupling is accounted for. CeSn_3 provides a most interesting case study here as the mixed valence material whose Fermi surface is known [14]. Band structure calculations find a Fermi surface in reasonable agreement with the deHaas-vanAlphen measurements yet produce a density of states too small to account for the specific heat by a factor of 5-7 [15]. This claim that the Fermi surface is in good agreement has been criticized [16] but a more careful extraction of the Fermi surface has shown that the agreement is actually excellent except for a slight discrepancy in a small spool-shaped structure located at M which is not part of the f-orbital derived surfaces at Γ and R. (This discrepancy appears to arise from the omission of

the non-spherical terms inside the muffin-tin spheres.) The large difference between the specific heat and the density of states remains independent of the choice of exchange-correlation functional and is much too large to ascribe to electron-phonon interactions. The words one will hear in discussing this are "electron-electron interactions" and "spin fluctuations." A useful aspect to focus on here is that missing from this description are the low lying LOCAL excitations of the system. Note that to get at the poorly screened peak, it was necessary to break the symmetry and use an impurity-like description. These f-electron systems have a large reservoir of rather local states just above the Fermi energy because only a few of the 14 f-orbitals are occupied. And although the occupied f-states have developed some dispersion, the states above the Fermi energy have very little dispersion in most cases. An examination of a density of states curve for a Ce or light actinide compound will clearly show two spin-orbit split peaks just above the Fermi energy with a tail of spectral density pulled to and below the Fermi energy. It is this tail that gives rise to the occupied f-orbital in Ce and the ~ 2.5 f-electrons in U compounds. Cognizance should thus again be taken of the local excitations. The ground state is not exhibiting this character as seen from the fact that the Fermi surface is given correctly. This can be illustrated using the following results. NpSn_3 has a rather large specific heat even when the critical fluctuations of the antiferromagnetic phase transition are discounted. Yet, a moderately straightforward if arduous band structure calculation [17] yields excellent results for the specific heat both in the paramagnetic and antiferromagnetic phases. In studying the systematics of the U Ll_2 structured materials [18], it is found that USn_3 has very large enhancements similar to CeSn_3 (See Fig. 1) where USi_3 and UGe_3 do not. The density of states in USn_3 has risen over that of USi_3 and UGe_3 but not enough

to account for the large increase in specific heat. The band density of states is reasonable as it agrees with the high temperature specific heat analysis [19]. Thus, one has the picture of a reservoir of states in the U and Ce compound that is not present in the Np compound [20] unless one counts the magnetic critical fluctuations.

Thus far, localization of excited states has been advanced as a critical topic. This should not be taken to imply that localization is not to be seen in the ground state. The lattice constant analysis of mixed valence is immediate evidence to the contrary. The volume collapse of Am under pressure [21] is another. One of the features observed from the calculation of equilibrium lattice constants is that as the f-orbital is becoming very localized, the LDA is not sufficiently localizing the orbital. Thus, it is often necessary to insert the localization by hand which does produce quite respectable results. An excellent example is CeSb in its field-induced ferromagnetic state where a reasonable representation of the Fermi surface is only obtained by artificially decoupling the f-state, putting it in an assumed crystal field state, and then treating it as an external driving force to the remaining conduction electrons [22]. The origin of the difficulty is the lack of a term driving the system towards integral occupation. Thus the LDA, and at least some more complex density functional theories, will put half an electron on each of the nuclei in the H_2^+ ion at large separation--just as will the Hartree-Fock.

While it is actually the localization of the excited state which is more crucial than that in the ground state, the two are not unrelated. It is productive to examine the nature of the ground state. Two very interesting classes of materials are based on the cubic Laves phase and the Cu_3Au crystal structures which are discussed below.

THE CERIUM CUBIC LAVES PHASE MATERIALS

A very interesting feature of the AB_2 type cubic Laves structured compounds is that the A sublattice is a diamond structure. This diamond structure has been observed to have some strong bonding properties for d-orbitals [23]. Another interesting feature of this structure is that the sphere sizes are separately determined by the A-A and the (very close) B-B contact distances. In the Np materials of this phase, it was observed that the f-orbital atoms (which are invariably on the A sublattice) occur very close together such that one might expect the direct interaction between f-orbitals on adjacent atoms forming a "pure" f-band. The Np Laves phases actually span the critical separation for this interaction and were analyzed as such [24]. This is the same elementary physics that led Hill to make his interatomic correlation plots. A modified form of such a plot is shown in Fig. 2 for Ce. The basic assumption of such plots is that local moment magnetism could be characterized by its transition temperature (T_N or T_C) and that superconductivity was its antithesis which could be represented by its transition temperature plotted in the opposite direction. Magnetism is taken to be the signature of localization, and superconductivity as the ultimate signature of delocalization. This rough index was taken as the ordinate with the f-atom separation as the abscissa because the small f-orbitals must be brought close together if they are to interact. In the close separation regime, the correlation works perfectly: There are no magnetic materials except where there is iron or nickel present to drive it. Of course, because a direct f-f interaction is not the only possible interaction the f-orbital can have, not all materials at large separation are localized systems. The heavy fermion materials all fall in this class, for example. Many of the Ll_2

structured materials also fall in this class--that has been the origin of interest in them, in fact. It is quite interesting to ask whether such an analysis should also apply to the Ce Laves phases with the smaller 4f orbital. Certainly, one has both types of properties since CeRu_2 and CeCo_2 are superconductors and CePt_2 is magnetic. The critical separation appears to be too small relative to other structures but one must recognize that the coordination number is small (4). Making a standard metallurgical correction to CN12, the critical separation falls more in line. It is this modified form of a Hill plot given in Fig. 2.

The diamond structure should be especially favorable for the xyz (i.e., A_{2u} or Γ_2') type f-orbital to form a direct f-f bond as it is directed along the $\langle 111 \rangle$ near neighbor directions. Thus, the band results for these compounds are examined for occupied f-orbital character of this type. The partial density of states for CeRu_2 is shown in Fig. 3 as a representative material. The first thing to note is that there is virtually NO occupied A_{2u} character. The occupied f-character is of the T_{1u} and T_{2u} type and is spread down through the d-bands of the Ru. This is also observed for CeNi_2 , CeCo_2 , CeRh_2 , CeOs_2 , and CeIr_2 . Thus, although the Ce atoms are close enough for direct f-f interactions, they are preempted by a coupling to the transition element d-orbitals. This can be further illustrated by a simple computer experiment. If the 4f states are not permitted to be present by selecting 5f states in the basis set, the f-charge is reduced by only about half. Thus, although there is a tremendous energy penalty (about 50 eV) in selecting the f-character, the boundary conditions set up by the B-atom d-states are very strong and drive the Ce atom.

In light of these results, why should a Hill plot find a transition to magnetic behavior in CePt_2 at roughly a separation in accord with other

materials? Part of the answer lies in the fact that it only occurs if one has made the correction to CN12. But that can only be at best part of the story in light of the strong d-orbital driving force observed. (An attempt to perform a calculation for CePt_2 in the paramagnetic state failed because of wild oscillations in the SCF process.) And what of the Np materials? That remains to be investigated, of course, but it should be noted that Np has a lot more f-character which is the more extended 5f. These results for Ce only heighten the curiosity as to their nature in the light actinides. For example, how much f-character might one find in ThRu_2 ? These are truly interesting materials in which to examine the interplay between two possible interaction mechanisms.

THE L1_2 (Cu_3Au) STRUCTURED MATERIALS

The L1_2 structured materials have been advanced as an excellent set of systems to study materials systematics germane to the properties of f-orbital localization and thereby the phenomenon of mixed valence and heavy fermion behavior [18]. The structure is not a favorable one for superconductivity but one gets close. UPu_3 is a superconductor--although not heavy. UPt_3 is a heavy fermion superconductor but has transformed to a related hexagonal phase (similar to the fcc to hcp transformation). CePb_3 is nominally a heavy fermion antiferromagnet that becomes superconducting in an applied field. There are also a number of disordered alloys that superconduct. The structure does display antiferromagnetism-- CePb_3 , UPb_3 , and NpSn_3 are all good examples. It also has examples of heavy fermion behavior-- CePb_3 , NpSn_3 , and $\text{U}(\text{Sn}_{2/3}\text{In}_{1/3})_3$. To these, it is appropriate to add the interstitial alloys--especially CePd_3B_x . The crystal structure is actually quite easy to visualize. One starts with an fcc lattice but converts the face centered

atoms to another type. Because there are three times as many face centered atoms as corner atoms, one arrives at the characteristic AB_3 formula. This is like the relation of the CsCl lattice to the bcc structure. In the $L1_2$ structure, the A atoms have 12 B type nearest neighbor atoms, thus satisfying the requirement for high coordination number prevalent in the heavy fermion materials. The B atoms have 8 B and 4 A atoms in the nearest neighbor shell. For p-electron atoms such as the group IV's, this presents a dilemma to the p-orbitals in that they have directional flexibility to either form p-p bonds within the B sublattice or p-f bonds with the A sublattice, but not both! This situation can be correlated to the systematics of these materials [24]. In particular, as one moves down the series from USi_3 to UPb_3 , one will find the p-p bond becoming stronger at the expense of the f-p bond leaving the f-orbital uncoupled. This makes for a very plausible explanation of the behavior observed in Fig. 1: For the smaller Si and Ge, the p-f bond is forced and the materials behave in a standard band manner. For the larger Sn and Pb atoms, the p-p bond comes into play and the f-orbital is more isolated. These materials have recently all been recalculated keeping the spin-orbit coupling in a fully relativistic calculation at all steps by making use of the quaternion formulation of the generalized eigenvalue problem [25]. (The materials involved were $CeSn_3$, $CePb_3$, $CeRh_3$, $CePd_3$, USi_3 , UGe_3 , USn_3 , UPb_3 , URu_3 , URh_3 , and UIr_3 .) It was found that the density of states at the Fermi energy was unaffected for the important case of $CeSn_3$, but were in most cases increased. In Table I, the charge analysis of the almost normal metal like USi_3 is compared to that of USn_3 and paramagnetic UPb_3 . The significant thing to note is that there is more f-charge in USn_3 and UPb_3 which is much closer to an $f_{5/2}$ orbital. The smaller f-count in USi_3 accompanies an increased Si p-count through the formation of hybrid orbitals. The greater

admixture of $f_{7/2}$ character occurs because the admixed orbitals are more spin states than j states. Both changes are thus consistent with the USn_3 and UPb_3 having much more local f -character.

Table I. Charge Analysis for USi_3 , USn_3 , and Paramagnetic UPb_3
(fully relativistic results for vonBarth-Hedin exchange-correlation)

	<u>USi_3</u>	<u>USn_3</u>	<u>UPb_3</u>
a	7.6333	8.74	9.05
E_F	0.722	0.536	0.471
$n(E_F)$	33.8	66.	1~77.
Us	0.15	0.21	0.24
$Up_{1/2}$	0.07	0.08	0.07
$Up_{3/2}$	0.33	0.20	0.16
$Ud_{3/2}$	0.61	0.58	0.62
$Ud_{5/2}$	0.50	0.63	0.56
$Uf_{5/2}$	1.40	2.10	2.27
$Uf_{7/2}$	0.78	0.57	0.42
Xs	1.33	1.47	1.64
$Xp_{1/2}$	0.65	0.67	0.81
$Xp_{3/2}$	1.25	1.09	0.91

The transition metal systems such as URh_3 and UIr_3 involve the d -orbitals and should be different. However, not as different as might be thought at first glance. In the related case of UPt_3 , it is really the p -orbitals that broaden

the f-orbitals [26]. The primary effect of the d-orbital admixture is to pull spectral weight from the buried d-bands up to the Fermi energy. The transition metal d-bands are found below the Fermi energy even for URu_3 and the Fermi energy is in the regime of the nearly free electron like plane wave band of the pure transition metal. Being the upper half of this band, it is predominantly p-like. This view makes the interstitial alloy URh_3B even more interesting. Initially, it had been hoped that the addition of B (which goes in at the cube center so one ends up with an inverted Perovskite structure) would provide adequate localization to induce a second poorly screened peak. This did not happen even though the f-peak was narrowed dramatically [27]. But now that material should be examined to determine the mechanism of the narrowing. Is it merely the lattice constant expansion or an alternate coupling for the Rh p-orbitals? The Rh compound will have greater d-orbital contribution than the Pt because the Rh d bands are much closer to the Fermi energy and the f's. Experience with the SCF process of CeRh_3 and CePd_3 offers an intriguing aspect. In the latter stages of the SCF process, both materials experienced f to d charge fluctuations but the mechanism was quite different. In CeRh_3 , this was effected by fluctuations in the relative admixture of f-character into the individual eigenfunctions. The major effect in CePd_3 was in the choice of occupied states. The individual eigenfunctions were much less affected. The d-f hybridization, which is larger in CeRh_3 , is clearly more sensitive to the state of the system. What about URh_3 ? Clearly we know a great deal about URh_3 itself [28]. To examine the pressure dependence and also be of use in discussing the boron alloy system, a calculation was also performed for a slightly expanded lattice constant. The charge decomposition of these calculations are compared to that of URh_3B in Table 2. Again the calculations are fully relativistic carrying the spin-

orbit coupling throughout the SCF process. Several things become obvious. Expanding the lattice increases the U f- and d-character and decreases the Rh d- character at a rate slightly faster than would extrapolate to the lattice constant of URh_3B . The uranium f- character is much closer to a $f_{5/2}$ state in URh_3B --a clear signature of greatly reduced hybridization. The Rh p-character has not significantly diminished with expansion but is reduced in the boron material. This cannot be claimed to prove anything but it is certainly highly suggestive.

Table II. Charge Analysis for URh_3 and URh_3B (Fully Relativistic
Calculation with Exchange Only)

	<u>URh_3</u>	<u>$\text{URh}_3(\text{exp.})$</u>	<u>URh_3B</u>
a	7.542	7.600	7.823
z_F	0.745	0.706	0.816
$n(E_F)$	34.1	34.4	~130
Us	0.21	0.24	0.37
$\text{Up}_{1/2}$	0.03	0.08	0.13
$\text{Up}_{3/2}$	0.23	0.23	0.27
$\text{Ud}_{3/2}$	0.51	0.56	0.64
$\text{Ud}_{5/2}$	0.61	0.61	0.79
$\text{Uf}_{5/2}$	1.22	1.33	1.94
$\text{Uf}_{7/2}$	0.71	0.74	0.49
Rhs	0.50	0.49	0.35
$\text{Rhp}_{1/2}$	0.16	0.15	0.11
$\text{Rhp}_{3/2}$	0.31	0.30	0.22
$\text{Rhd}_{3/2}$	3.07	3.05	2.90
$\text{Rhd}_{5/2}$	4.31	4.26	4.10
Bs	**	**	0.51
$\text{Bp}_{1/2}$	**	**	0.25
$\text{Bp}_{3/2}$	**	**	0.48

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REFERENCES

- [1] D. D. Koelling, Rep. on Prog. Phys. 44, 139 (1981)
- [2] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)
- [3] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)
- [4] N. D. Mermin, Phys. Rev. 137, A1441 (1965)
- [5] A. K. Theophilou, J. Phys. C: Solid St. 12, 5419 (1979)
- [6] W. Kohn and P. Vashishta, in Theory of the Inhomogeneous Electron Gas, [N. H. March and S. Lundqvist, ed.]
- [7] J. C. Slater, Adv. Quantum Chem. 6, 1 (1972)
- [8] J. F. Janak, Phys. Rev. B 18, 7165 (1978)
- [9] B. W. Veal and P. Paulikas, Phys. Rev. Lett. 51, 1995 (1983)
- [10] M. R. Norman, D. D. Koelling, and A. J. Freeman, Phys. Rev. B 31, 6251 (1985); and 32, 7748 (1985)
- [11] W. E. Pickett, A. J. Freeman, and D. D. Koelling, Physica 102B, 341 (1980) (See Fig. 2)
- [12] R. Zeller and P. H. Dederichs, Physica 130B, 34 (1985)
- [13] L. J. Sham and W. Kohn, Phys. Rev. 145, 516 (1966)
- [14] W. R. Johanson, G. W. Crabtree, A. S. Edelstein, and O. D. McMasters, Phys. Rev. Lett. 46, 504 (1981)
- [15] D. D. Koelling, Sol. St. Comm. 43, 247 (1982)

- [16] P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J. W. Wilkins,
Comments in Solid State Physics 12, 99 (1986)
- [17] M. R. Norman and D. D. Koelling, Phys. Rev. B (in press)
- [18] D. D. Koelling, B. D. Dunlap, and G. W. Crabtree, Phys. Rev. B31, 1966
(1985)
- [19] M. R. Norman and S. D. Bader, Phys. Rev. B (in press)
- [20] M. R. Norman and D. D. Koelling, Physica 135B, 95 (1985)
- [21] H. L. Skriver, O. K. Andersen, and B. Johansson, Phys. Rev. Lett. 44,
1230 (1980)
- [22] M. R. Norman and D. D. Koelling, Phys. Rev. (in press)
- [23] D. D. Koelling, D. L. Johnson, S. Kirkpatrick, and F. M. Mueller, Sol.
St. Commun. 9, 2039 (1971)
- [24] A. J. Arko and D. D. Koelling, Phys. Rev. B 17, 3104 (1978)
- [25] J. J. Dongarra, J. R. Gabriel, D. D. Koelling, and J. H. Wilkinson,
J Comp. Phys. 54, 278 (1984)
- [26] R. Albers, Phys. Rev. B 32, 7646 (1985)
- [27] Z. Zolnierrek, A. J. Arko, and D. D. Koelling, 5f-Band Narrowing in UX3B
Compounds: Evidence from Resonant Photoemission, Conf. on Basic and
Applied Research on Actinides and Their Compounds, Future Prospects,
Carnot aix-en-Provence, France, Sept. 1-6, 1985
- [28] A. J. Arko, D. D. Koelling, and J. E. Schirber, Handbook on the Physics
and Chemistry of the Actinides, vol.2, A. J. Freeman and G. H. Lander
[ed], North Holland, 1985

LIST OF FIGURES

- Fig. 1. Comparison of electronic specific heat coefficient to density of states for the isoelectronic sequence USi_3 , UGe_3 , USn_3 , and UPb_3 . The calculated UPb_3 value is for the paramagnetic phase and would be much reduced in the observed antiferromagnetic phase. The "experimental value" for UPb_3 is not real but merely a prediction following the observation in $NpSn_3$.
- Fig. 2. Modified Hill plot for Ce. A metallurgical correction to effective radius for a coordination number of 12 has been applied for the cubic Laves phase materials.
- Fig. 3. Partial density of states for $CeRu_2$. (a) Ce f states in the A_{2u} representation showing the lack of these $\langle 111 \rangle$ directed states. (b) Ce f states in the T_{1u} representation. (c) Ce f states in the T_{2u} representation. (d) Ru T_{2g} d-states. (e) Ru E_g d-states.

Specific heat (γ)

Fig. 1

Fig. 2.

CeRu₂

Atom Type 1 A2U

CeRu₂

Atom Type 1 TiU

CeRu₂

Atom Type 1 T2U

Partial Density of States

Fig. 3c

CeRu₂

Atom Type 2 T2G

CeRu₂

Fig. 3e