

Electronic band-structure hybridization in the heavy-fermion superconductor UPt_3

R. C. Albers

Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 15 July 1985)

Many physical properties, such as electrical resistivity and specific heat, of UPt_3 are different from the other two heavy-fermion superconductors, UPe_3 and CeCu_2Si_2 . The electronic structure of UPt_3 also differs from the other two materials because of the presence of the platinum d band, which is close in energy to the uranium $5f$ band that is responsible for the exotic heavy-fermion ground state. In this paper various contributions to linear muffin-tin orbital atomic-sphere approximation electronic band-structure calculations are examined to show that platinum p hybridization is the dominant platinum hybridization mediating the formation of the uranium $5f$ band. The main effect of uranium $5f$ and platinum $5d$ hybridization is instead to induce platinum d character at the Fermi energy that would otherwise be absent, while having little effect on the uranium $5f$ band itself. Any experiment, such as soft-x-ray emission, resonant photoemission, or nuclear magnetic resonance that can probe this platinum d character could yield an important confirmation of itinerant uranium f electrons.

Heavy-fermion systems exhibit a variety of unusual and exotic ground states.¹ These states are almost surely dominated by the strong electron-electron correlations that are not included in normal density-functional electronic band-structure calculations. Nonetheless, these exotic correlated ground states must form out of a typical metallic one-electron-like state as the temperature is lowered, and it is therefore important to examine and understand the physics of this "normal" state. Also, since there are many possible low-temperature ground states for heavy-fermion materials, some peculiarity in the normal-state properties could cause electron-electron correlations to favor one ground state over another.

The focus of this paper is on one-electron hybridization and especially its effects on the uranium $5f$ electron-band in UPt_3 , because this band is almost certainly responsible for the exotic low-temperature properties. The UPt_3 system itself is of special interest among heavy-fermion materials because of the possible coexistence of spin fluctuations and superconductivity² as well as the general possibility that UPt_3 is a p -wave superconductor.³

Of the three known heavy-fermion superconductors (UPe_3 and CeCu_2Si_2 are the other examples), UPt_3 is different. For example, the UPt_3 electrical resistivity decreases monotonically as the temperature is lowered rather like a normal metal, whereas the other two systems show a far more complex temperature dependence, which are quite similar to each other. Other differences are reviewed in Ref. 1. In terms of one-electron structure, one might readily assume that these differences are due to the platinum $5d$ bands, since UPe_3 and CeCu_2Si_2 have no d bands anywhere near the Fermi energy E_F (the fully occupied Cu d bands in CeCu_2Si_2 are well below the Fermi energy⁴). In platinum metal E_F cuts across the top of the $5d$ band, which therefore plays a significant role in the physical properties of platinum. Because platinum makes up 75% of UPt_3 , one might expect a similar situation.

However, while explicit calculation (see below) shows a filled platinum $5d$ band, nonetheless, these bands are still sufficiently close to the Fermi energy that their effects on the uranium $5f$ band (which is pinned to E_F by Coulombic energy considerations) demand careful investigation.

Figure 1 shows the total density of states (DOS) of UPt_3 as calculated by the linear-muffin-tin-orbital⁵ (LMTO) scalar-relativistic electronic band-structure method in the atomic-sphere approximation (ASA) with a Barth-Hedin exchange-correlation potential. The density of states was calculated by the tetrahedron method⁶ with 175 k points in the irreducible part of the Brillouin zone for the final converged iterations and for the plots shown in this paper. Equal atomic sphere radii ($S=3.0488$ bohrs) were used for the uranium and platinum sites in order to reduce overlap of the atomic spheres. The calculations were done for the experimentally observed hexagonal SnNi_3 structure (eight atoms per unit cell, two equivalent uranium and six equivalent platinum sites).

We have also done more detailed calculations^{7,8} including the combined correction term⁵ as well as fully relativistic (including spin-orbit) calculations, as have others.^{9,10} While these additional effects are important for obtaining an accurate one-electron picture of the UPt_3 electronic structure, our interest here is solely to understand the important influences within the one-electron structure, for which the ASA approximation is sufficiently accurate.

The overall features of the electronic structure are clear from Fig. 1. From approximately -8 to -1 eV there is a large broad peak in the DOS due to the platinum $5d$ bands. Above these bands are broad platinum $6s$ - $6p$ bands and uranium $6d$ - $7s$ bands. While the uranium $6d$ is mainly above E_F it hybridizes with the platinum d bands causing a hybridization gap or relatively low DOS near E_F . The uranium $7p$ and platinum $5f$ sit very high in energy above E_F and play no role. The dominant feature of the electronic structure is, of course, the enor-

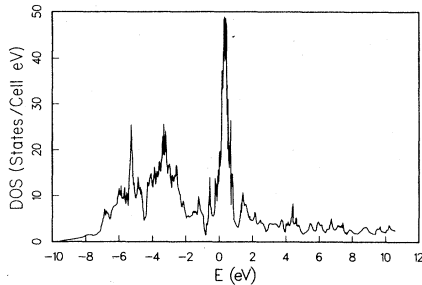


FIG. 1. Fully hybridized density of states for UPt_3 in the SnNi_3 lattice structure. The calculations were done by the LMTO ASA electronic band-structure method. The zero of energy in the figure is the Fermi energy of the fully hybridized calculations. The density of states (DOS) is the complete density of states including all uranium and platinum contributions and all angular momentum components.

ous DOS of the narrow uranium $5f$ band, which is pinned to E_F . Because the U-U atomic separation is large¹¹ and hence the overlap of the uranium wave functions is correspondingly small, it is necessary to study the hybridization with the surrounding platinum atoms in order to understand the formation of an uranium $5f$ -band-like state.

Within the ASA approximation the influence of the platinum atoms on the uranium $5f$ band can be studied by selectively turning on uranium $5f$ hybridization with different platinum angular momentum components. The results of such calculations (more specific details about this procedure are given below) are shown in Figs. 2 (a) and (b), which focus on the relevant uranium f -projected DOS. As expected, the unhybridized $5f$ band is very narrow, with a bandwidth $W_f \sim 0.2$ eV compared with the fully hybridized result of $W_f \sim 0.8$ eV. Turning on hybridization with platinum d states shifts the center of the f band to higher energies and produces an additional high energy tail in the projected f DOS. The width of the central peak remains at about 0.2 eV. The hybridization with platinum p states, in contrast, causes a dramatic broadening of the uranium $5f$ band. While the remaining hybridizations are necessary to get the details of the band structure exactly right (the platinum d hybridization, e.g., is necessary to center the band at higher energies), Fig. 2 (a) suggests that the platinum p hybridization is the dominant effect controlling the band formation of the uranium $5f$ itinerant states.

Two major consequences follow from this: (i) UPt_3 is similar to other heavy-fermion systems in that the band formation of the f states is mediated by broad s - p bands of neighboring atoms. (ii) The platinum $5d$ bands seem less likely as a candidate to explain differences between UPt_3 behavior and other heavy-fermion superconductors and suggests that more attention be given to other possible candidates, such as the closer uranium spacing of UPt_3 .

In addition to the results of Fig. 2, platinum s hybridization, which has even less effect than platinum d hybridization in broadening the uranium $5f$ band, as well as various combinations of different kinds of hybridization such as simultaneous platinum s and d hybridization have

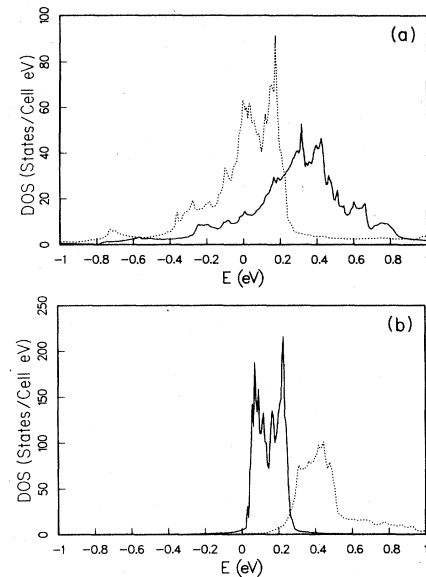


FIG. 2. (a) Uranium f projected density of states for fully hybridized calculations (solid line) and for uranium f and platinum p hybridized calculations (dashed line). The zero of energy is the same as Fig. 1. (b) Uranium f projected density of states for unhybridized calculations (solid line) and for uranium f and platinum d hybridized calculations (dashed line). The zero of energy is the same as Fig. 1.

also been examined. Hybridization between uranium f and uranium s , p , and d states are of course ineffective because of the large U-U atomic separation. In all these cases, the results are similar to Fig. 2, i.e., a combination involving platinum p hybridization is necessary to sufficiently broaden the central f -DOS peak to compare favorably with the fully hybridized result. Similar calculations for a hypothetical cubic Cu_3Au crystal structure (which differs from the observed hexagonal Ni_3Sn structure by the usual fcc-versus-hcp stacking of atomic planes) resembled those of Fig. 2, except for a slight enhancement of the effects of the platinum p hybridization.

Because of the nearness of the filled platinum d band to the uranium f band and to the Fermi energy, it is also important to understand how this d band hybridizes and is otherwise influenced by the uranium atoms. Figures 3(a) and (b) show the effects of uranium- $6d$ -platinum- $5d$ hybridization, where all other hybridization is turned off. Unlike pure uranium metal, in UPt_3 the uranium $6d$ band sits relatively high in energy (about 2 eV above the Fermi energy). For this reason the uranium and platinum d hybridization is relatively weak, each inducing a small density of states in the region of the other band. The main part of the density of states for each band is almost identical in position and magnitude with the corresponding unhybridized bands. A hybridization gap with essentially zero density of states occurs between the platinum and uranium d bands

In contrast to this weak d - d hybridization, Fig. 4 shows the effect of uranium $5f$ and platinum $6d$ hybridization on the platinum $6d$ band. While this f - d hybridization has little effect on the uranium $5f$ band as discussed

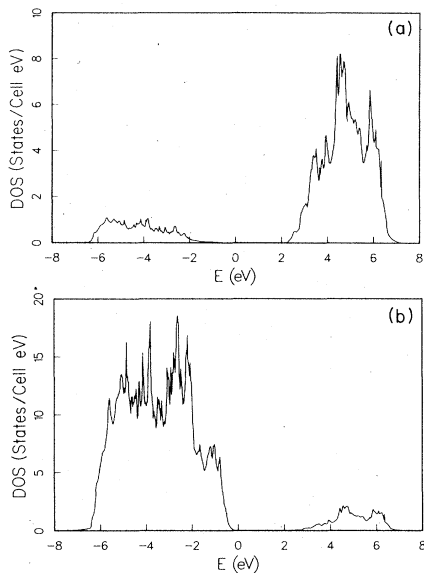


FIG. 3. (a) Uranium d projected density of states for calculations that only allow hybridization between uranium d and platinum d states. The zero of energy is the same as Fig. 1. (b) Platinum d projected density of states for calculations that only allow hybridization between uranium d and platinum d states. The zero of energy is the same as Fig. 1.

above, the effect on the platinum d character is dramatic. A relatively large peak in the platinum d density of states is induced in the region of the uranium $5f$ band. Since this density of states is not present in the absence of itinerant uranium $5f$ electrons (this has also been confirmed by other fully-relativistic calculations, not shown here,⁷ where three uranium f electrons have been forced into the core and only s - p - d orbital angular momentum components were included in the basis set of the bands), this suggests that any experiment that shows an enhanced platinum d character at the Fermi energy would provide strong additional evidence for itinerant f character in UPt_3 . Soft-x-ray emission to the platinum $4f$ core states ($\text{N VI}-\text{N VII}$ emission), resonant photoemission, or nuclear magnetic resonance are some possible experiments where one might look for such effects.

The techniques used to generate Figs. 2–4, i.e., turning various hybridizations on and off as desired, demonstrate the usefulness of the ASA approximation of Andersen⁵

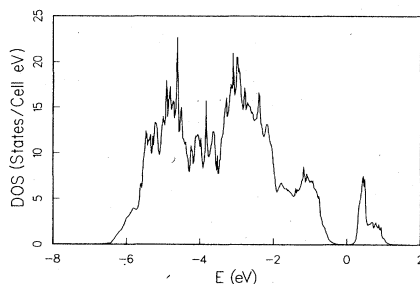


FIG. 4. Platinum d projected density of states for calculations that only allow hybridization between uranium f and platinum d states. The zero of energy is the same as Fig. 1.

for understanding electronic band-structure results. Instead of obtaining the final results in one complicated calculation, one can easily break up the calculation into components and look for the underlying physics in each. These same techniques of course apply to other compounds than just UPt_3 . In principle, similar techniques could also be developed for other band structure methods such as Korringa-Kohn-Rostoker (KKR), for example.

Within the ASA approximation, the band-structure eigenvalues and wave functions for a Bloch wave vector \mathbf{k} are determined by diagonalizing Hamiltonian H and overlap O matrices, which, for compounds, may be schematically indicated by

$$\langle t'q'm' | (H - EO) | t'l'q'm' \rangle. \quad (1)$$

Here t specifies the inequivalent atoms of the compound (in UPt_3 the uranium and platinum sites), q specifies a specific atom in the unit cell (e.g., which of two equivalent uranium sites or six equivalent platinum sites), and lm the standard angular momentum labels. For UPt_3 this is a 128×128 matrix for each \mathbf{k} vector. The simplicity and elegance of the ASA is derived from the way that the dependence on the radial potential is confined to a set of five potential parameters for each inequivalent type of atom, whereas the geometry of the crystal lattice only enters the Hamiltonian and overlap matrices through a set of structure constants $S_{LL'}^k$ (where I have used L as an abbreviation for $tlqm$). Because of this one may easily turn off hybridization for different inequivalent atom types and angular momentum components by setting the structure constants to zero for whatever off-diagonal components ($L \neq L'$) one does not wish to couple. In principle this allows one to block diagonalize different pieces of the matrices separately. That is, instead of diagonalizing one huge 128×128 matrix, one may diagonalize matrices whose dimensions are determined by the number of l and t components that are coupled together.

In our case, the ASA program was modified to allow all diagonal components $t=t'$ and $l=l'$, while zeroing all off-diagonal components. This guarantees that the determinants of our matrices will always be nonzero and hence the single diagonalization of the ASA program works normally, in this case simultaneously generating all the unhybridized bands. Since all the different bands are decoupled from each other, one may focus on any band of interest, the uranium $5f$ band in our case. The different platinum hybridizations can then be turned on one by one and their effect on the uranium $5f$ band examined by zeroing all off-diagonal elements $L \neq L'$ of the structure constants, except for those couplings under investigation.

In conclusion, it has been shown that the dominant interaction controlling the formation of the normal-state uranium $5f$ bands in UPt_3 is the uranium $5f$ and platinum $6p$ hybridization and is not hybridization with the platinum $5d$ bands, as intuition would suggest. The main effect of the uranium $5f$ and platinum $6d$ hybridization is instead to induce a platinum d character at the Fermi energy that would otherwise be absent. Soft-x-ray emission, resonant photoemission, nuclear magnetic resonance, or any other experiment capable of probing this induced platinum d character would therefore be a useful test to

demonstrate itinerant f -electron character at the Fermi energy in UPt_3 .

ACKNOWLEDGMENTS

I am especially indebted to J. L. Smith for helping to focus and clarify the ideas in this paper. I also thank A.

M. Boring, A. C. Lawson, J. O. Willis, and others at Los Alamos National Laboratory for their helpful suggestions as well as D. D. Koelling at Argonne National Laboratory and P. Weinberger at the Technical University of Vienna.

-
- ¹G. R. Stewart, *Rev. Mod. Phys.* **56**, 755 (1984); F. Steglich, U. Ahlheim, J. J. M. Franse, N. Grewe, D. Rainer, and U. Rauchschwalbe, *J. Magn. Mater.* (to be published); Z. Fisk, H. R. Ott, and J. L. Smith, *J. Magn. Mater.* **47-48**, 12 (1985).
- ²G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, *Phys. Rev. Lett.* **52**, 679 (1984).
- ³The other heavy-fermion superconductors may also be p wave. See also D. J. Bishop, C. M. Varma, B. Batlogg, and E. Bucher, *Phys. Rev. Lett.* **53**, 1009 (1984); J. P. Rodriguez, *Phys. Rev. Lett.* **55**, 250 (1985); S. N. Coppersmith and R. A. Klemm, (unpublished).
- ⁴T. Jarlborg, H. F. Braun, and M. Peter, *Z. Phys. B* **52**, 295 (1983).
- ⁵O. K. Anderson, *Phys. Rev. B* **12**, 3060 (1975); H. L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).
- ⁶O. Jepsen and O. K. Anderson, *Solid State Commun.* **9**, 1763 (1971); G. Lehman and M. Taut, *Phys. Status Solidi B* **54**, 469 (1972).
- ⁷R. C. Albers, A. M. Boring, and N. E. Christensen, *Bull. Am. Phys. Soc.* **30**, 523 (1985), and unpublished.
- ⁸A. M. Boring, R. C. Albers, F. M. Mueller, and D. D. Koelling, *Physica* **130B**, 171 (1985).
- ⁹P. Strange and B. L. Gyorffy, *Physica* **130B**, 41 (1985). T. Oguchi and A. J. Freeman, *Bull. Am. Phys. Soc.* **30**, 356 (1985).
- ¹⁰Electronic band-structure results for the heavy-fermion superconductor UBe_{13} have been reported in Ref. 8 as well as by T. Takegahara, H. Harima, and T. Kasuya, *J. Magn. Mater.* **47-48**, 263 (1985).
- ¹¹For UPt_3 , $CeCu_2Si_2$, and UBe_{13} , the respective f -atom separations are 4.1, 4.1, and 5.1 Å. Thus UPt_3 has a much smaller U-U separation than UBe_{13} . Because the $4f$ atomic wave functions are much less spatially extended than the $5f$ wave functions, the effective f -atom separation in UPt_3 is also smaller than for $CeCu_2Si_2$. That is, the effective overlap of the f wave functions at the Ce separation in $CeCu_2Si_2$ would correspond to a much larger uranium separation in UPt_3 .