RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 11 1 DECEMBER 1985

Soft-x-ray emission intensities in UIr_3, UPt_3, and UAu_3

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(Received 20 August 1985)

The $N_{6,7}$ emission spectra of Ir, Pt, and Au in the compounds UIr_3, UPt_3, and UAu_3 have been calculated. These calculations were performed with use of the fully relativistic self-consistent linear muffin-tin orbital (LMTO) band results for the densities of states and the LMTO potentials to calculate the radial transition probabilities and emission spectra. An induced Pt d character at E_F that is just above the main part of the Pt $5d$ band and is due to U $5f$–Pt $5d$ hybridization is found and shows up as a shoulder on the high-energy tail of the $N_{6,7}$ spectra in this system. The calculations lead to different spectra in each material reflecting the difference in the $5d$ states in each material due to changes in the position and strength of hybridization to the U $5f$ band. Because the induced Pt d electronic structure occurs only through hybridization with itinerant U $5f$ electrons and is absent for localized U $5f$ electrons, an experimental check of these results for UPt_3 is important.

INTRODUCTION

There is much interest in the electronic structure of heavy-fermion systems.[1] One of the more unusual heavy-fermion systems is UPt_3, which shows both superconductivity and spin fluctuations.[2] Evidence for spin-fluctuation behavior is a $T^3 \ln T$ term in the low-temperature specific heat, a feature which disappears around 0.5 K when the resistivity goes to zero. Because both superconductivity and spin fluctuations occur, the possibility of p-wave or triplet-pairing superconductivity has been suggested[2,3] for these systems.

This possibility of a new class of superconductors has led to many experimental and theoretical studies of this system. Because of the strong electron-electron correlations in this system, it appears that most of the physical properties at low temperature are dominated by the electronic structure. Band-structure calculations have been performed to determine this electronic structure.[4–6] In addition, there have been many experimental probes of this electronic structure.

The band-structure calculations show a narrow U $5f$ band near the Fermi energy (E_F) with a bandwidth broader than that suggested by some experimental results,[7] but narrower than that seen in others,[8] that is generated by the U f–Pt p hybridization.[9] The Pt d band, which is not filled in Pt metal, becomes filled by charge transfer and hybridization with the U. A hybridization gap is created between the Pt $5d$ states (below E_F) and the U $6d$ states (above E_F). However, the U $5f$–Pt $5d$ hybridization induces Pt $5d$ states into this gap at E_F.[9] It has been suggested that it is these states that are superconducting.[10]

One experimental probe that may be able to see these induced Pt $5d$ states is the $N_{6,7}$ soft-x-ray emission spectra (Pt $5d_{5/2,3/2}$ electrons decaying into Pt $4f_{7/2,5/2}$ core holes and emitting an x ray). For that reason we have calculated this emission spectrum. In order to have comparison spectra, we have also calculated the soft-x-ray spectra of UIr_3 and UAu_3. This set of compounds has E_F moving across the top of the $5d$ band. For in UIr_3 the Ir site has one less $5d$ electron, and so one would not expect the Ir $5d$ band to be filled. Hence, the U $5f$ band, which is pinned to E_F by Coulombic energy considerations, sits at the top of the Pt $5d$ band and is greatly broadened by very strong hybridization compared to its width in UPt_3 and UAu_3. The other extreme is UAu_3, where one would expect a completely filled $5d$ band (for the metal) well below E_F and a Au $5d$–U $6d$ hybridization gap to appear near E_F (but not at the same position as in UPt_3). UPt_3 is a borderline case where the filled Pt $5d$ band appears to be just barely below the U $5f$ band and E_F.

METHOD

The $N_{6,7}$ spectra of the pure Au and Pt metals have been calculated previously using a fully relativistic approach.[11,12] These results were in excellent agreement with the experimental results for these metals.[12] In addition, the $N_{6,7}$ emission spectra have been calculated for the Au_xPt_{1-x} alloys.[13]

Allowing only electron dipole transitions, the intensity for emission is given by

$$I_j^\alpha(E) \sim (\Delta E)^3 \sum_{\kappa'} (2j+1) \begin{pmatrix} j & 1 & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} R^{\alpha}_{\kappa\kappa'}(E_j^\alpha, E) N^{\alpha}_{\kappa'}(E) , \tag{1}$$

where E_j^α is the jth core level of the αth atom ($\kappa = -1-1$ for $j = 1+\frac{1}{2}$; $\kappa = 1$ for $j = 1-\frac{1}{2}$). The radial transition probabilities are given by

$$R^{\alpha,j}_{\kappa,\kappa'}(E_j^\alpha, E) = \int r^3 [f^\alpha_\kappa (E_j^\alpha, r) f^\alpha_{\kappa'}(E,r) + g^\alpha_\kappa (E_j^\alpha, r) g^\alpha_{\kappa'}(E,r)] dr , \tag{2}$$

where f and g are solutions to the radial Dirac equation. In Eq. (1) $N^\alpha_{\kappa'}(E)$ is the local partial density of states (DOS) for the αth atom and is obtained from a band calculation.

These expressions were evaluated for the Ir, Pt, and Au $N_{6,7}$ spectra using the potentials and DOS functions obtained from fully relativistic linear muffin-tin orbital (LMTO) self-consistent calculations for UIr_3, UPt_3, and UAu_3.[5] The results for UIr_3 and UAu_3 were obtained for these crystals in the Cu_3Au structure (UIr_3 forms in the Cu_3Au structure and the structure of UAu_3 is unknown but most likely not Cu_3Au). For UPt_3 the calculations were performed for the Ni_3Sn crystal structure (the observed structure). For all three systems the same volume per molecular unit was used and it was chosen to be that of UPt_3. The experimental molecular volume for UIr_3 is actually 8% smaller than that of UPt_3.

RESULTS AND DISCUSSION

Table I shows the relativistic selection rules for the N_6 and N_7 emission processes. As was shown earlier,[13] the radial transition probabilities for Au and Pt (and the same is true for Ir) are monotonically increasing functions of the energy which have no structure, so the structure in the emission spectra should reflect the structure in the partial DOS functions. In Fig. 1 the separate N_6, N_7, and the total $N_{6,7}$ calculated spectra are shown for all three systems. These spectra were obtained by folding the bare intensities with a Lorentzian function with a half-width of 0.5 eV to simulate a 0.5-eV detector resolution. The $5d$ DOS near E_F is reflected in the high-energy features of the N_6 and N_7 spectra. Because of the spin-orbit splitting of the $4f$ states and the selection rules, the high-energy N_7 spectra (short-dash–long-dash curve) falls in the lower-energy part of the N_6 spectra and is completely masked. However, the high-energy features of the N_6 can be seen in the high-energy tail of the total emission. In UIr_3 it is seen that the high-energy tail is rather smooth with no sharp features. For UPt_3 a small shoulder has developed, and in UAu_3 this feature becomes a separate small peak. In Fig. 2 the changes in the emission spectra of UPt_3 with decreasing detector resolution is given. Given the good agreement between the calculated and measured $N_{6,7}$ spectra in pure Au and Pt, one might expect that the high-energy features could be seen in a detector with better than 0.6-eV resolution.

TABLE I. Selection rules for N spectra.

	Core state	Valence state	Δ_j[a]
N_6	$4f_{5/2}$	$d_{3/2}, d_{5/2}$	0, ±1
N_7	$4f_{7/2}$	$d_{5/2}$	±1

[a] The $\Delta_j = 0$ transition is forbidden nonrelativistically.

In order to understand these spectra, we show in Fig. 3 the $5d_{3/2}$ and $5d_{5/2}$ Ir, Pt, and Au projected DOS functions

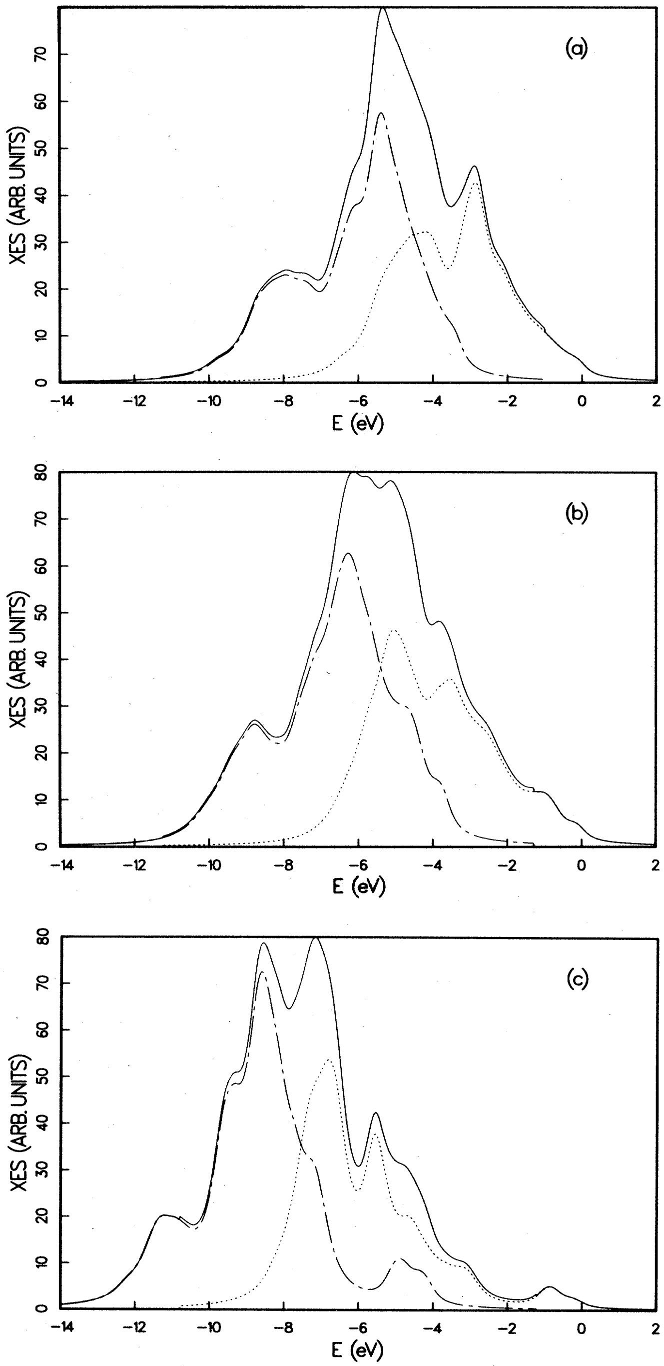

FIG. 1. Theoretical $N_{6,7}$ spectra for (a) Ir, (b) Pt, and (c) Au in UIr_3, UPt_3, and UAu_3. The full curves correspond to the superposition of the N_7 (short-dash–long-dash) and N_6 (dotted) spectra. The zero of energy for each material corresponds to the energy cutoff at E_F. All spectra have 0.5-eV Lorentzian broadening.

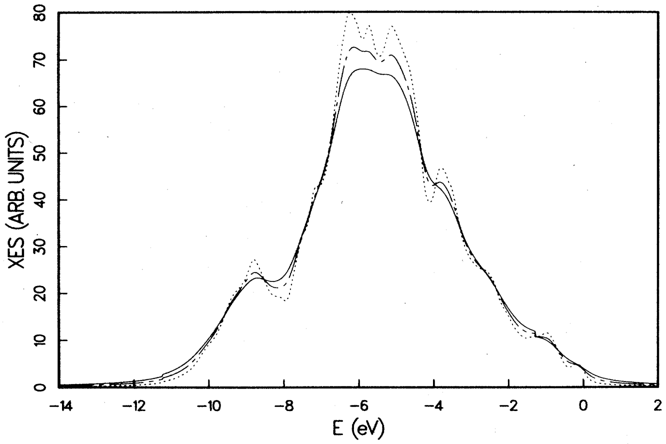

FIG. 2. Theoretical $N_{6,7}$ spectra for Pt in UPt$_3$ The spectra correspond to three different Lorentzian broadenings. The dotted curve has a broadening of 0.25 eV, the short-dash–long-dash curve has 0.50-eV broadening, and the full curve corresponds to 0.75-eV broadening.

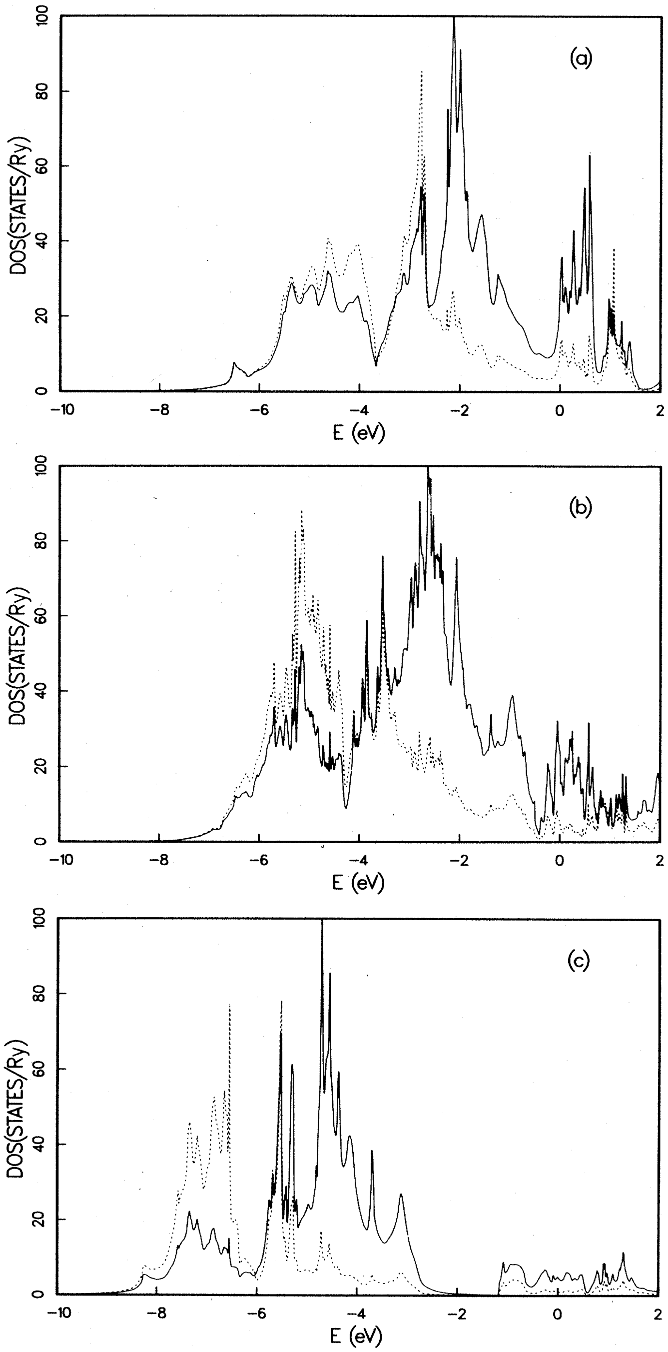

FIG. 3. The $5d_{3/2}$ (dotted) and $5d_{5/2}$ (solid) DOS functions in (a) UIr$_3$, (b) UPt$_3$, and (c) UAu$_3$. The zero of energy is at E_F in each material.

for the respective compounds. For either d-DOS functions, one observes a normal d-band DOS with two additional peaks on the high-energy side of the plots. These additional peaks are at exactly the same positions as the U $5f_{5/2}$ and U $5f_{7/2}$ bands for each compound. As shown in Ref. 5 if one does a band-structure calculation with the U $5f$ electrons forced into the core as localized electrons and the band structure is only allowed to contain s-p-d angular momentum components, these additional two peaks in the transition-metal DOS are removed. Hence, this additional high-energy two-peak structure is induced by hybridization with itinerant U $5f$ electrons.

In UIr$_3$, the U $5f$ band is located at the top of the Ir d band. The strong hybridization induces a low-energy tail in the U f-projected DOS function. Most of occupied part of the U f electrons are in this low-energy tail and hence the two large peaks in the U f DOS are mainly above E_F, unlike UPt$_3$ and UAu$_3$. Hence, the Ir $N_{6,7}$ spectrum misses the induced and unoccupied Ir d structure due to these peaks and has a rather smooth high-energy tail.

In UPt$_3$, the U $5f$ band sits adjacent to but above the Pt d band greatly reducing the hybridization. The U $5f$ low-energy tail is smaller and most of the U f DOS are in the lower part of the $5f_{5/2}$ peak. The induced Pt d DOS reflects this peak and shows up as a shoulder in the Pt $N_{6,7}$ spectra. For UAu$_3$ the d band has dropped well below E_F and the induced Au d character shows up as a well-separated peak in the Au $N_{6,7}$ spectra.

In all the transition-metal d bands shown, the $d_{5/2}$ projected DOS is greatly enhanced over the $d_{3/2}$ projected DOS in the region of the U f bands near E_F. This is because the $d_{5/2}$ band is closer in energy to the U f bands and hybridizes more strongly with them. It is unfortunate that the high-energy side of $d_{5/2}$ DOS is in the N_7 spectra and completely masked by the low-energy part of the N_6 spectra, since the induced platinum d DOS leads to a much larger feature in the N_7 spectra.

CONCLUSIONS

Although we have focused on the high-energy tail of the $N_{6,7}$ spectra, since this gives some information about the Pt $5d$ DOS which is induced by the U $5f$ itinerant states near the Fermi energy, it would also be of interest to have the experimental $N_{6,7}$ spectra for these materials for the overall placement of the $5d$ states. Since the difference in hybridization of these $5d$ states with the $5f$ states (in the different systems) is what may determine the electronic structure, the agreement between theory and experiment on the overall $5d$ electronic structure may be as important as the fine details near E_F. It is hoped the $N_{6,7}$ spectra will be obtained experimentally in some or all of these systems soon.

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[7] From the specific-heat data it has been suggested that the $5f$ is of the order 0.05 eV wide, whereas the band calculations tend to give widths an order of magnitude larger. See Ref. 1.

[8] From the photoemission studies on UPt_3 the $5f$ states are seen spread over 5 eV—an order of magnitude larger than calculated.

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