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Electronic structure and optical properties of $ThPd_3$ and UPd_3

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We present calculations of the electronic and optical properties of the actinide compounds $ThPd_3$ and UPd_3 using the state-of-the-art full-potential linearized augmented-plane-wave method as implemented in the WIEN97 code. Both compounds crystallize in the complex $TiNi_3$ structure with 16 atoms per unit cell. For comparison with earlier work, we also studied these compounds in the $AuCu_3$ structure. However, we find that the results in this hypothetical structure do not compare that well with experiments as in the actual $TiNi_3$ structure. We have calculated the density of states (DOS), the coefficient of the electronic specific heat, and the frequency-dependent optical conductivity. These quantities are compared with experiments where good agreement is obtained. The DOS is dominated by Pd d states below the Fermi energy and by actinide f states near and above the Fermi energy. Transitions between these states dominate the optical conductivity and we find that the optical matrix elements do not play an important role. This finding is supported by experiments on a comparison of x-ray photoemission spectroscopy (XPS) data with optical conductivity.

I. INTRODUCTION

The existence of $5f$ electrons in actinide compounds has given rise to the seemingly perpetual question of whether these states are localized, intermediate-valent, or itinerant. These compounds are particularly interesting as they bridge the gap between the itinerant $3d$ electrons in transition metals and the localized $4f$ electrons in rare earths. Much work has already been done in order to understand the behavior of $5f$ electrons in actinide compounds.[1] Hence there exists a general interest in $5f$ systems from the experimental as well as the theoretical side. UPd_3 with the electronic configuration of $5f^3 6d^1 7s^2$ has been a subject of several experimental studies using different techniques. Some of these are resistivity studies,[2] electron-spin-resonance (ESR) measurements,[3] neutron scattering,[4] susceptibility measurements,[5,6] low-temperature specific-heat measurements,[6,7] photoemission,[8] optical measurements,[9] and Fermi-surface measurements.[10] Most of these studies agree on an f^2 configuration of a U^{4+} ion with complicated phase transitions at very low temperatures.[11,12] Hence, the literature on UPd_3 contains a wealth of experimental data. However, many fewer theoretical studies have been published. Earlier theoretical studies on UPd_3 mainly consist of electronic-structure calculations by Norman *et al.*[13] and by Eriksson *et al.*[14] Norman *et al.*[13] have performed calculations for the experimentally observed $TiNi_3$ (DO_{24}) structure of UPd_3 using the linear muffin-tin-orbital (LMTO) method in the atomic-sphere approximation (ASA), where the $5f^2$ electrons have been treated as core states. They have calculated the DOS and the Fermi surface. Their DOS compares well with experiments except for the peak position corresponding to the localized f level. They have presented the DOS in arbitrary units and did not deduce the electronic specific-heat coefficient. Their Fermi surface of UPd_3 shows reasonable agreement with experimental data but has some additional undesirable features. They find that it is necessary to shift bands in order to get quantitative agreement with experiment. Other attempts to improve the calculations such as inclusion of $l=3$ basis functions, use of an exchange-only functional, and addition of combined correction terms had little effect. Naturally, the discrepancy is thus suspected to be due to inadequacies of the local-density approximation (LDA) in correctly placing the d bands with respect to the s-p bands or, more likely, due to the ASA. These authors have also studied UPd_3 earlier[15] in the $AuCu_3$ structure as part of an investigation of the electronic structure and properties of UX_3 ($X=\mathrm{Ru, Rh, Ir, Pt}$) compounds. The other work[14] has focused on the electronic structure of ARh_3 ($A=$actinide) systems and the $5f$ localization in UPd_3 using both the scalar-relativistic as well as the fully relativistic LMTO-ASA method. In order to understand the effect of ligand states on the nature of $5f$ electrons in U, they calculated the electronic structure for UM_3 ($M=$Mo to Ag) compounds. All of these materials, except UPd_3, crystallize in $AuCu_3$ structure, hence UPd_3 was also studied in this space group to facilitate that kind of comparison. They[14] obtained a much smaller theoretical equilibrium volume for UPd_3 than the experimental value and found UPd_3 to be stable in a ferromagnetic state even at highly compressed volumes. Experimentally, magnetic order has been found below 4.5 K,[11,12] where the magnetic moment was reported to be extremely small.

In this work, we present results on electronic structure and optical properties of $ThPd_3$ and UPd_3, two actinide–transition-metal intermetallic compounds. We have used the state-of-the-art full-potential linearized augmented-plane-

TABLE I. Atomic positions in units of lattice parameter a in internal coordinates for $X\mathrm{Pd}_3$ compounds ($X=\mathrm{U, Th}$) in TiN_3 structure.

Atom	Wyckoff position	Position in the unit cell
$X1$	$2a$	0.0 0.0 0.0
$X2$	$2d$	$\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{4}$
Pd1	$6g$	$\frac{1}{2}$ 0.0 0.0
Pd2	$6h$	$\frac{5}{6}$ $\frac{2}{3}$ $\frac{1}{4}$

wave (FP-LAPW) method[16] including spin-orbit interaction with the generalized gradient approximation (GGA) and thus avoid shortcomings as present in the previous ASA-based LMTO calculations. Our results are compared to experimental data on specific heat,[6,7] XPS,[8,17] as well as optical conductivity.[9,18]

II. METHOD AND CRYSTAL STRUCTURES

The calculations are performed using the FP-LAPW method as is implemented in the WIEN97 code,[19] including local orbits for the high-lying "semicore" states. Exchange and correlation are treated in the generalized gradient approximation (GGA) within density-functional theory[20] using the parametrization of Perdew *et al.*[21] Core states are treated fully relativistically,[22] while for the valence states, spin-orbit interaction is added in a second variational step using the scalar-relativistic orbitals as a basis.[23] The DOS has been calculated using the modified tetrahedron method of Bloechl *et al.*[24] The frequency-dependent optical properties are obtained using the joint density of states (JDOS) weighted by the dipole matrix elements[25] of the optical transitions. We also include intraband transitions using a lifetime broadening of 0.01 eV. The TiNi_3 structure is hexagonal and thus the optical conductivity has two components, σ_{xx} and σ_{zz}. Since the experimental data for these compounds have been measured on polycrystalline samples, we present also an average over the two components, $(2\sigma_{xx}+\sigma_{zz})/3$. UPd_3 and ThPd_3 crystallize in hexagonal TiNi_3 (DO_{24}) structure with 16 atoms per unit cell.[26] We use the experimental lattice constants[26] $a=11.065$ a.u. and $c=18.568$ a.u. for ThPd_3 and $a=10.879$ a.u. and $c=18.181$ a.u. for UPd_3. These lattice constants are almost the same as the latest.[27] In the unit cell of $X\mathrm{Pd}_3$, we have two nonequivalent X atoms and two kinds of Pd sites (see Table I).

In order to study the influence of the crystalline environment, and for comparison with earlier work,[14,15] we also performed calculations for ThPd_3 and UPd_3 in the hypothetical AuCu_3 crystal structure. In these calculations, we adopted the same volume per formula unit resulting in lattice constants of 7.895 a.u. for ThPd_3 and 7.752 a.u. for UPd_3. These calculations have been converged with 84 k points in the irreducible ($\frac{1}{48}$th) Brillouin zone, whereas we used 76 k points in the irreducible ($\frac{1}{24}$th) Brillouin zone of the TiNi_3 structure. In the AuCu_3 structure, each atom X ($X=\mathrm{Th, U}$) has 12 equivalent nearest Pd neighbors, while in the TiNi_3 structure only six Pd atoms surround the X atom and there are two different kinds of X and Pd atoms. Therefore, we can expect different properties of the compounds in the two crystal structures.

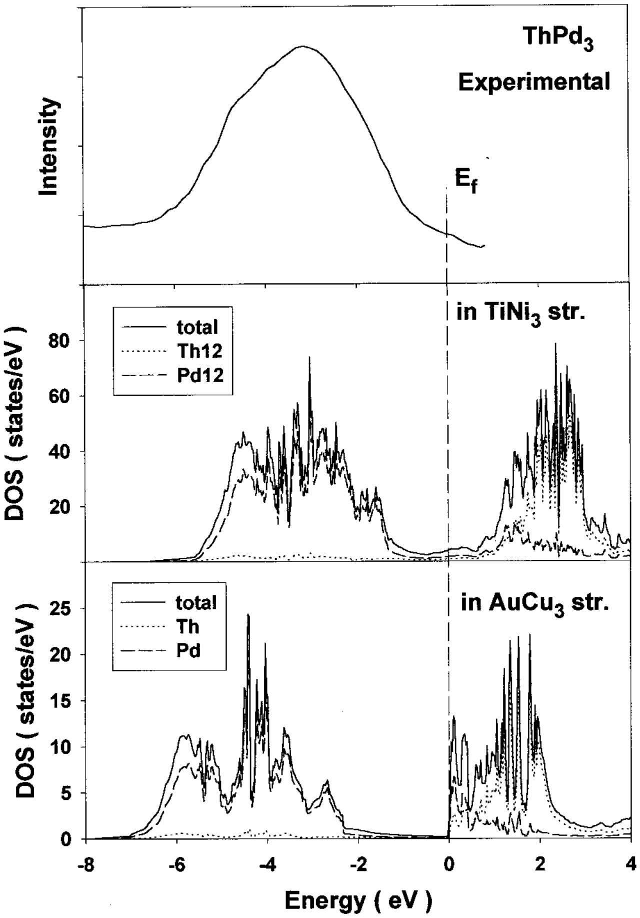

FIG. 1. The XPS data for ThPd_3 (top) in arbitrary units, calculated total and partial DOS for ThPd_3 in TiNi_3 structure (middle), and in AuCu_3 structure (bottom). The E_f is set to 0.0 eV.

III. RESULTS AND DISCUSSION

A. ThPd_3 in the TiNi_3 structure

The total DOS and partial DOS for ThPd_3 are displayed in Fig. 1 along with the measured XPS spectrum.[17] The DOS of ThPd_3 is dominated by contributions from Th f and Pd d states, and only these contributions are displayed together with the total DOS in Fig. 1. The DOS for the Pd1 and Pd2 sites is not much different and thus only the sum is shown. These states dominate from 5.5 to 1.5 eV below the Fermi energy (E_f) but there are also some Pd d contributions to the unoccupied DOS up to 2 eV above E_f, which has also significant Th d contributions. The main peak at about 3 eV above E_f comes of course from Th f states, which are completely empty as expected from the electronic configuration of Th. The two Th sites have slightly different charges and thus the main $5f$ peaks between 2 and 3 eV above E_f have more Th1 contributions at higher energies. In the experimental XPS data,[17] we find a structure at 2 eV, the main peak at 3 eV, and a shoulder around 4.5 eV below the Fermi level. These features may correspond to peaks around 1.8, 3, and 4.5 eV, respectively, below E_f in the theoretical DOS in reasonably good agreement with the experimental data. The total DOS at the E_f is 3.95 states/eV cell. The corresponding coefficient of the electronic specific heat is 2.33 mJ/mol K^2 compared to the experimental value[6] of 1.5 mJ/mol K^2. The

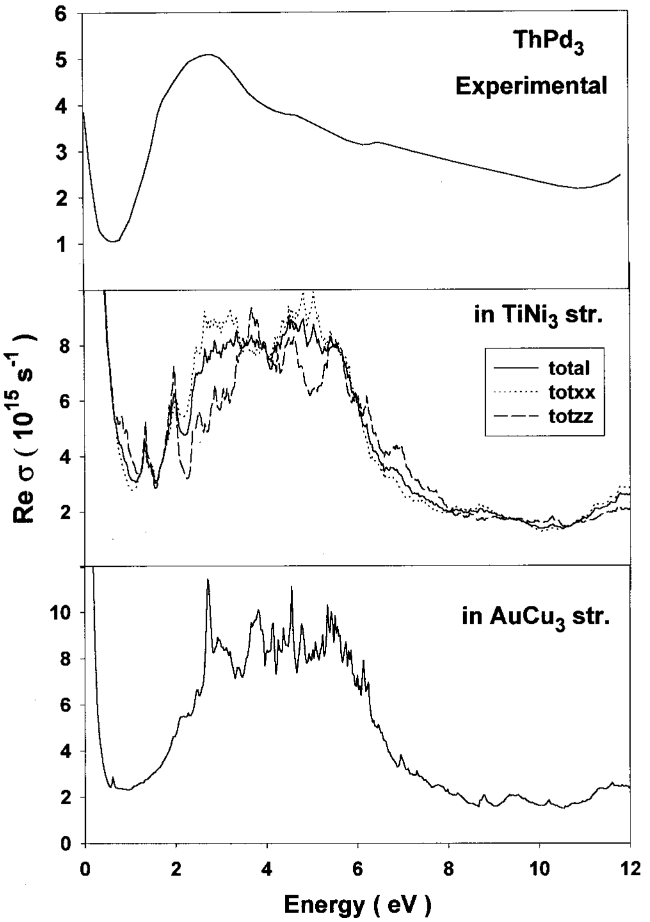

FIG. 2. Real part of the frequency-dependent optical conductivity for ThPd$_3$: experimental curve (top), calculated [in TiNi$_3$ structure (middle) and in AuCu$_3$ structure (bottom)].

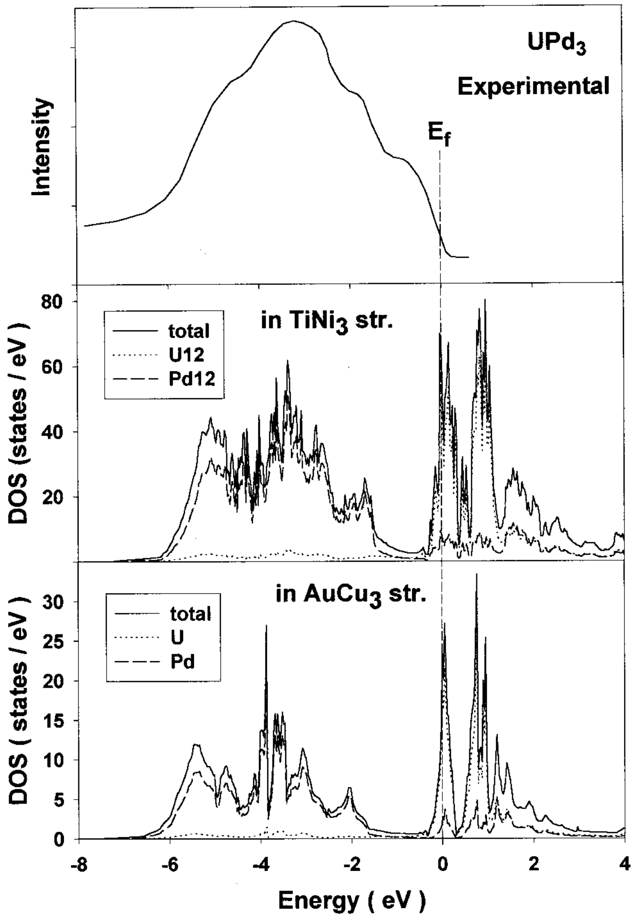

FIG. 3. The XPS data for UPd$_3$ (top) in arbitrary units, calculated total and partial DOS for UPd$_3$ in TiNi$_3$ structure (middle), and in AuCu$_3$ structure (bottom). The E_f is set to 0.0 eV.

theoretical value is larger than the experimental one and this seems to suggest that localization effects play a significant role here.

The total DOS concentrates in two main regions: one between 1.5 and 5.5 eV below E_f due to Pd d states, and another one between 1 and 3 eV above E_f due to Th f states. Transitions between these regions yield the main contribution to the frequency-dependent optical conductivity. The real part of the calculated frequency-dependent optical conductivity, σ, for ThPd$_3$ is displayed in Fig. 2 along with the experimental curve.[18] Our curve is too peaky as compared to the experimental curve as we have included very small lifetime broadening. The theoretical curve starts with a sharp drop and a dip at about 1 eV followed by a steep rise and a structure at about 2 eV culminating into the main peaks, which are broad and centered around 3 and 5 eV. Then it falls sharply with a shoulder at about 6.6 eV. After this there is a steady decrease and a dip at about 10 eV and a rise thereafter. The optical conductivity has a noticeable anisotropy and σ_{xx} shows a more pronounced double-peak structure (at 3 and 5 eV), while σ_{zz} has its main peak around 3.8 eV. The general features of the theoretical curve are similar to the experimental spectrum,[18] but our main feature is broader. The dip at 10 eV and the upturn for higher energies is present in both. To study the effect of the dipole matrix elements for the optical conductivity, we also calculated the JDOS. Interestingly, the JDOS is quite similar to the optical conductivity (hence we choose not to show the JDOS), indicating that for this compound the selection rules do not play an important role. This is in agreement with the observation of Schoenes and Andres from a comparison of their optical conductivity data[9,18] with the XPS data[8,17] that the matrix elements for the transitions play a minor role in determining the spectra of these compounds. Hence there is an overall fairly good qualitative as well as quantitative agreement with the experimental data for the calculated DOS, coefficient of electronic specific heat, and optical conductivity of ThPd$_3$.

B. UPd$_3$ in the TiNi$_3$ structure

Next we discuss our results for UPd$_3$. The calculated total DOS and the partial DOS together with the experimental XPS data[8] are illustrated in Fig. 3. As in ThPd$_3$, the main contributions below E_f come from Pd d states, whereas the DOS at and above E_f is dominated by U f contributions. Both Pd1 and Pd2 DOS are similar and overlap, hence only the sum is displayed in the figure. For UPd$_3$, the f DOS for the U1 and U2 sites are quite similar; however, in contrast to ThPd$_3$, these exhibit a much more pronounced splitting into U f $\frac{5}{2}$ and $\frac{7}{2}$ states of the main peak above E_f observed in the total DOS. The DOS between 1.5 and 6 eV below E_f has mainly Pd d character, whereas the large peaks around E_f

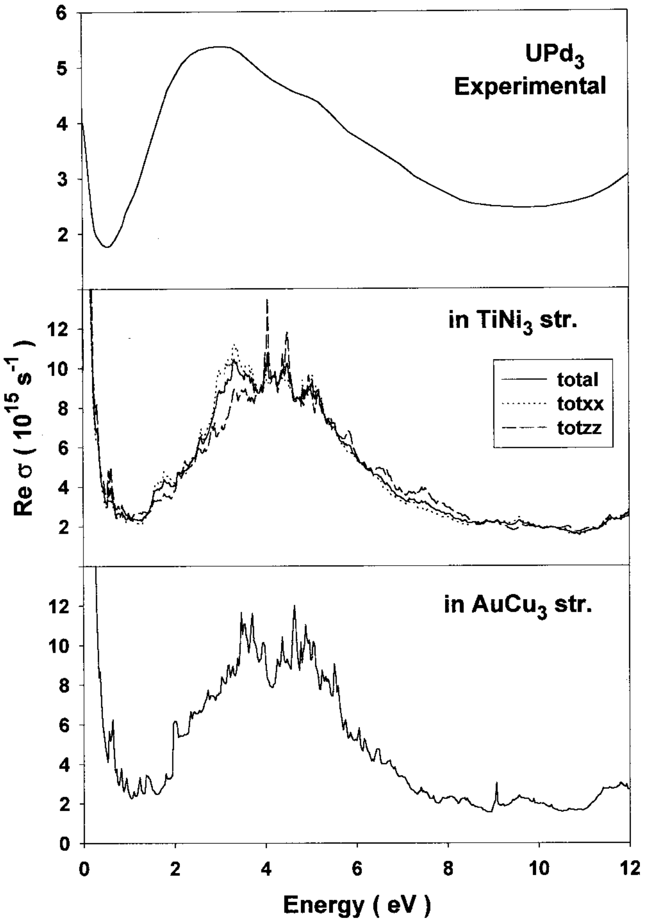

FIG. 4. Real part of the frequency-dependent optical conductivity for UPd_3: experimental curve (top), calculated [in $TiNi_3$ structure (middle) and in $AuCu_3$ structure (bottom)].

originate mainly from U f states, indicating partially filled U f states. The smaller peaks beyond 1.6 eV above E_f are mainly from U d states with a strong admixture of Pd d. Comparing the total DOS with the experimental XPS spectrum,[8] we find that the calculations can reproduce most of the experimental features showing structures at 1.0, 2.0, 2.9, 4.6, and 5.0 eV below E_f. The only exception is that the theoretical DOS (Fig. 3) has a strong peak at E_f but no feature around 1 eV below E_f, which is also absent in the work of Norman *et al.*[13] They obtained a localized U f peak at 2.5 eV below E_f, which does not show up in the experimental data. As expected, for density-functional theory (DFT) calculations we find all the U f states around E_f. The total DOS at E_f is 68.2 states/eV cell (with a large uncertainty due to the spiky DOS structure and the limited k mesh in the DOS calculation), which yields a γ value of 40.3 mJ/mol K^2 for UPd_3. The specific heat for UPd_3 has been measured by Andres *et al.*[6] and Zaplinski *et al.*[7] Although it is difficult to separate the linear part from the total specific heat because of phase transitions near 7 K, the γ was estimated to be between 4 and 10 mJ/mol K^2. Our value is, as in $ThPd_3$, much larger than this experimental estimate and indicates that the $5f$ states cannot be described properly by an itinerant (delocalized) picture.

The real part of the theoretical σ of UPd_3 in $TiNi_3$ structure is presented in Fig. 4 together with the experimental[9] curve. In the calculated σ, we find structures starting at around 2 eV, a broad main peak ranging from 3 to 5 eV, followed by a shoulder above 7 eV and a broad dip ranging from 8 to 11 eV. The general shape of the experimental spectrum (top of Fig. 4) agrees quite well with the theoretical curve. The major difference is that the theoretical main peaks are broader and shifted to slightly higher energies compared to experiment, and that the experimental feature at 5 eV is much weaker than in theory. The experimental XPS spectra[8] and the optical conductivity[9] of UPd_3 have a remarkable similarity, which suggests that the final states of the optical transition must be very close to E_f and also that the dipole matrix elements for transition are not playing a significant role. These observations are in accordance with our findings that the JDOS is quite similar to the optical conductivity (which includes these matrix elements). Similar to $ThPd_3$, we conclude that the transitions from Pd d states to U f states govern the optical conductivity of UPd_3.

Comparing our results for $ThPd_3$ with those for UPd_3, we find that the $5f$ states are unoccupied in $ThPd_3$ and are well above E_f. This results in a much smaller DOS at E_f in agreement with experiment. For UPd_3, the U $5f$ states are right at E_f, resulting in a large γ value. The occupied Pd d DOS is slightly different for the two compounds and in particular the unoccupied actinide d/Pd d band is below the dominant $5f$ peak in $ThPd_3$ while it is above it in UPd_3.

C. $ThPd_3$ and UPd_3 in the hypothetical $AuCu_3$ structure

Since most of the UM_3 compounds crystallize in the $AuCu_3$ structure, we have also investigated $ThPd_3$ and UPd_3 in this structure. Total-energy calculations verify, however, that the $TiNi_3$ structure is more stable by 4.7 (14.6) mRy per formula unit for $ThPd_3$ (UPd_3) in agreement with experiment. Nevertheless, we discuss here the calculations in the hypothetical $AuCu_3$ structure to check the effect of the crystal structure on the DOS and optical conductivity. The DOS for $ThPd_3$ and UPd_3 in $AuCu_3$ structure is shown in the lower panel of Figs. 1 and 3, respectively. A comparison with the calculated DOS in $TiNi_3$ structure shows that there are some differences in details of the DOS curves, but of course the general features of occupied Pd d states and (partly) unoccupied f states remain the same. The Pd d DOS below E_f is quite similar for both compounds in the $AuCu_3$ structure but is different from the corresponding DOS in $TiNi_3$ structure, implying that the Pd d states are affected differently in the two crystal structures. In addition, in $AuCu_3$ structure, they are shifted down in energy by about 1 eV, in disagreement with experimental XPS data. The largest difference is in the position of the Fermi level in $ThPd_3$, which is right at the beginning of the large peaks above E_f in $AuCu_3$ structure while it is 1 eV below those peaks in $TiNi_3$ structure. Comparing our DOS for UPd_3 in $AuCu_3$ structure with that from Eriksson *et al.*,[14] we find that there is a good qualitative agreement in the shape of the two DOS curves, but their DOS is spread over a larger energy region resulting in peak positions that are shifted away from E_f, both above and below E_f. We find the total DOS at E_f in $ThPd_3$ and UPd_3 in the $AuCu_3$ structure as 2.10 and 21.2 states/eV cell, respectively. (Note that here the unit cell contains only one formula unit compared to four in the case of $TiNi_3$ structure.) The corresponding γ values are 4.96 and 49.9 mJ/mol K^2, respectively, which are even larger than those in $TiNi_3$ structure.

The frequency-dependent optical conductivity of $ThPd_3$ and UPd_3 in the hypothetical $AuCu_3$ structure is shown in the lower panels of the Figs. 2 and 4, respectively. The calculated σ of $ThPd_3$ and UPd_3 is not very sensitive to the crystal structure, but the main peaks are even broader. In summary, we conclude that the hypothetical $AuCu_3$ structure does not represent faithfully the properties of these two compounds compared to the actual $TiNi_3$ structure. As expected, also in this structure the transitions from the Pd d states to the actinide f states dominate the optical conductivity, and σ with and without matrix elements turn out to be similar.

IV. CONCLUSIONS

In this work, the compounds $ThPd_3$ and UPd_3 have been studied in their experimentally verified $TiNi_3$ structure. The FP-LAPW method as implemented in the WIEN97 code has been used for these calculations. The ground state has been studied and very encouraging agreement with the experimental data for both compounds has been obtained for the DOS and the frequency-dependent optical conductivity. Our calculations show that the $5f$ bands in UPd_3 are partly occupied while those in $ThPd_3$ are completely empty. The DOS beyond 2 eV below E_f essentially arises due to Pd d states and is similar in $ThPd_3$ and UPd_3. The same is also reflected in the optical conductivity curves as the σ curves for the two compounds are similar in parallel with experiments. Most of the Pd d DOS is confined to the region below E_f and supports the conclusion of Schoenes and Andres[9] that the Pd d states are filled when Pd is alloyed with Th or U.

The optical conductivity shows only little changes when matrix elements are excluded. The same interesting feature is observed by comparing XPS data and experimental optical conductivity of these compounds.

On the other hand, we note that the experimental sigma of UPd_3 is broader than that of $ThPd_3$, but this is reversed in the calculation. Also, the coefficients of the electronic specific heat γ are much too large in these calculations compared to the experimental data, indicating that the $5f$ electrons are more likely localized and an itinerant description is not very suitable. This may be compared to a previous study[28] of the optical conductivity of the uranium monochalcogenides, of which UTe has nearly localized $5f$ electrons, where a number of features in the conductivity are explained but not all, substantiating the more localized nature of the $5f$ electrons.

We also studied these two compounds in the hypothetical $AuCu_3$ structure, as has been done for UPd_3 in earlier work,[14,15] to ascertain if the properties are affected significantly by crystal structure. Our results for UPd_3 in the $AuCu_3$ structure agree with the previous calculations. Although we do find an appreciable difference with the results from the actual $TiNi_3$ structure, we notice that this hypothetical structure does not yield as good an agreement for the DOS and frequency-dependent σ with the experimental data as the experimentally established $TiNi_3$ structure does. Hence the hypothetical simple $AuCu_3$ structure is not suitable for studying the properties of these compounds.

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