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Electronic structure calculations for actinide compounds

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Abstract. — In this paper we describe the use of muffin tin orbital techniques, employed in a variety of approximations, to help understand the band structure and bonding in actinide metals and compounds. Simple methods of assessing bandwidths and placings, readily accessible to experimentalists, are reviewed for both metals and compounds and their limitations discussed. Examples from the uranium monopnictides and chalcogenides, where a band structure approach is likely to be valid, are presented. Special emphasis is placed upon the mixing of the f-d bands of uranium with the p-bands of the pnictogen.

1. Introduction. — It has been generally accepted for some time [1] that light actinide conduction bands are derived from 5f, 6d and s-p electrons. In contrast in the transition metals and rare earths, the f-electron states are either not occupied or play only a small role in bonding respectively. In addition the division of the actinide metals into two groups (Th-Pu; Am and beyond) the first in which the f-electrons are in conducting and the second in which they are in non-conducting states suggests that the series may bridge a gap in properties between transition metals and rare earth metals [1].

The terms conducting and non-conducting states, rather than localized or itinerant states, are used advisedly in this paper since there is no reason why non-conducting states should not make significant contributions to chemical properties such as cohesion as there can be considerable overlap between Wannier functions on different sites. It happens that in the rare earths the f-electrons make little contribution to bonding (although overlap contributions to their crystal fields are thought not to be negligible [2]) and may therefore be described as localized or non-bonding and that the d-electrons of transitions metals are sometimes well described by pseudo-tight binding theories [3] especially when correlation effects are included in a local spin density approximation [4]. However in compounds of the transition metals there are many cases where non-conducting but bonding d-electrons may be found, nickel oxide being the best known example [5]. Since an energy band description of the actinides yields f-bandwidths spanning the range between heavy 3-d transition metals and light rare earths it is probably wise to keep these distinctions in mind.

Although correlation effects complicate the discussion of electronic properties of the light actinide metals they can be more important in the case of compounds. This is partly due to the fact that intrinsic f-bandwidths (i.e. due to direct f-f-overlap) normally narrow relative to the metallic bandwidth in compounds of a given metal, but also to the formation of bonds between the two components of the compound. There is evidence [6], however, that the variation of direct f-f-overlap in actinide compounds and intermetallics is responsible for behaviour best described sometimes by conducting and sometimes, by non-conducting f-electron states and that the actinide-actinide spacing is the important parameter determining such behaviour. Theoretical studies [7] of actinide systems with large actinide-actinide spacings suggest that intercomponent bonding in the compound also has a broadening effect upon f-electron states.

The attitude taken in this paper follows that of earlier energy band studies of the actinides [1] and rare earths [8] which is in the first instance to make an energy band calculation and to observe the width and extent of hybridization of f-electron states. Sometimes bands appear broad enough to suggest that correlation energies within the f-band have been sufficiently reduced compared with the f-bandwidth for a conduction electron theory to be plausible. If not, an alternative must be suggested.

In section 2 a simple scheme [9], which may be used to characterize bandwidths and placings for the
actinides and to compare them with other transitions series, is explained. In section 3 we discuss binary compounds and the uranium monopnictides and chalcogenides in particular with special emphasis upon the effects of uranium-uranium lattice spacing and the uranium-pnictogen bond. Finally in section 4 we again discuss correlation effects and conclude.

2. Features of f-bands in actinide metals. — It is possible to characterize, in a relatively simple way, the features of f-electrons in actinide metals and to show how they compare with the transition electrons of other series. To do this we shall use concepts developed from Linear Muffin Tin Orbital (LMTO) theory by Andersen [9, 10]. LMTO’s provide an energy independent basis set for the construction of Bloch functions and reduce the band structure problem to the non-standard eigenvalue problem. In general the method may be carried to an arbitrarily high degree of accuracy but an enormous simplification is obtained, with only slight loss of accuracy for at least simple metals, in the Atomic Sphere Approximation [10] (ASA) to the LMTO equations. In ASA one views the one conduction-electron problem as an eigenvalue problem for an atomic sphere, inside which the potential is spherically symmetric, subject to k-dependent and angular momentum destroying boundary conditions.

The k-dependent boundary conditions are contained in the structure constants $S_{i,L}$, which are essentially the zero energy limit of the KKR [11] structure constants and are independent of the scale of the structure. The information about the potential of the atomic sphere is contained, as usual, in the logarithmic derivative or phase shift. In ASA structural and potential information are completely separated and Andersen [9] has shown how the potential information may be listed in a set of four parameters $C_i, m_i, a_i, b_i$ for each value of angular momentum. Neither $a_i$ nor $b_i$ is negligible but they have been found to vary only slowly along the periodic table [12] and this remains true for the actinides. $C_i$ is the energy of the centre of the $i$th unhybridized band and $m_i$ is the band mass. The inverse of the band mass is proportional to the square of the amplitude of the wave function at the atomic sphere boundary. It is therefore a measure of the bandwidth of f-electron states.

With this simple picture it is possible to discuss not only complete band structures but, if elements of the structure constant matrix off-diagonal in angular momentum are set to zero, unhybridized bands whose widths are the result of direct overlap of wave functions of a given angular momentum. Further, the remaining diagonal blocks of the structure constant matrix may be diagonalized once and for all for a given structure producing a set of canonical bands $S_{i^*}^k$ from which the energy of unhybridized bands is developed from the expression

$$E_n^k = C_i + (1/\mu_i S^2) A_n^k, \quad S = \text{Wigner-Seitz radius}$$

$$A_n^k = S_n^k/(1 - \gamma_i S_k^*)$$

where $\gamma_i$ is a linear combination of the basic potential parameters (usually small) and anyway not ra-

| Table I. — Potential parameters for the d-transition series taken from Andersen and Jepsen (Ref. [12]). $C_i$ is the band centre and $\mu_i$ is the band mass. $S$ is the Wigner-Seitz radius in atomic units. |
|---|---|---|---|---|---|---|---|---|
| $3s^2 3p^6$ | $Sc$ | $Ti$ | $V$ | $Cr$ | $Mn$ | $Fe$ | $Co$ | $Ni$ |
| $(C_p - C_s) S^2$ | 7.427 | 7.367 | 7.317 | 7.207 | 7.147 | 7.017 | 6.967 | 6.917 |
| $C_s$ | 3.187 | 2.287 | 1.677 | 1.177 | 1.297 | 1.117 | 0.927 | 0.757 |
| $\mu_s$ | 0.747 | 0.717 | 0.707 | 0.707 | 0.737 | 0.757 | 0.777 | 0.807 |
| $\mu_p$ | 0.857 | 0.837 | 0.827 | 0.837 | 0.847 | 0.887 | 0.907 | 0.927 |
| $\mu_d$ | 5.607 | 5.967 | 6.287 | 7.147 | 8.277 | 9.877 | 11.37 | 13.27 |
| $4s^2 3d^{10} 4p^6$ | $Y$ | $Zr$ | $Nb$ | $Mo$ | $Tc$ | $Ru$ | $Rh$ | $Pd$ |
| $(C_p - C_s) S^2$ | 8.527 | 8.617 | 8.637 | 8.537 | 8.377 | 8.237 | 8.047 | 7.817 |
| $C_s$ | 4.077 | 2.797 | 1.847 | 1.217 | 0.747 | 0.337 | −0.047 | −0.097 |
| $\mu_s$ | 0.737 | 0.697 | 0.677 | 0.667 | 0.677 | 0.697 | 0.727 | 0.767 |
| $\mu_p$ | 0.817 | 0.777 | 0.767 | 0.767 | 0.777 | 0.797 | 0.817 | 0.857 |
| $\mu_d$ | 3.627 | 3.607 | 3.687 | 3.967 | 4.447 | 5.137 | 6.217 | 7.577 |
| $5s^2 4d^{10} 5p^6$ | $La$ | $Hf$ | $Ta$ | $W$ | $Re$ | $Os$ | $Ir$ | $Pt$ |
| $S$ (A.U.) | 3.624 | 3.301 | 3.069 | 2.945 | 2.872 | 2.825 | 2.835 | 2.897 |
| $C_s$ | 5.397 | 4.367 | 3.557 | 2.957 | 2.427 | 1.977 | 1.517 | 1.367 |
| $\mu_s$ | 0.787 | 0.737 | 0.717 | 0.707 | 0.717 | 0.737 | 0.767 | 0.817 |
| $\mu_p$ | 0.807 | 0.777 | 0.767 | 0.757 | 0.757 | 0.797 | 0.797 | 0.827 |
rapidly varying within a series, \( \mu_i = 2 m_i \), and is unity for free electrons. Thus the unhybridized bands are developed from the canonical bands by fixing the band energy, \( C_i \), scaling by the band mass \( m_i \) (or equivalently \( \mu_i \)) and distorting the bands by the parameter \( \gamma_i \) according to (1). Andersen [12] has listed the band mass \( \mu_i = 2 m_i \) for all the d-transition metal series. Part of this list is shown in table I. In order to make a comparison with the d-transition series we have computed the same parameters for some f-series metals and listed them in table II.

In making any comparison, however, one should note:

a) That Andersen's parameters were obtained using an \( X \approx 1 \) approximation [13], generally regarded to be better for lighter atoms in non-self consistent calculations whereas for the 4f's and 5f's we have used a local density approximation [14] which is almost identical to \( X \approx 2/3 \) [15] for the actinides. The use of \( X \approx 2/3 \) for the 4f's raises their energy and broadens the bands relative to the \( X \approx 1 \) band structure work for this series [8]. This is however advantageous since it makes the 4f band masses in table II a lower limit.

b) The variety of phases for the lighter actinide metals is difficult to deal with. We have therefore approximated by taking an fcc structure and an average lattice parameter of 4.8 Å for all of them. Similarly for the 4f's we have taken a hcp structure and average lattice parameter corresponding to an fcc parameter of 5.0 Å in order to make a direct comparison. Configurations are also doubtful for actinides so that we have made the calculation for uranium with both f' d' and f'' d'' configurations to show the kind of change that might be expected.

c) The parameters are, of course, sensitive to lattice parameter — therefore we show in table III the variation of potential parameters for uranium (f' d') with change of lattice parameter.

Table III. — Potential parameters as a function of lattice parameter for f' d' uranium in an assumed fcc structure.

| \( S \) (A.U.) | 3.40 | 3.55 | 3.69 | 3.98 |
| \( (C_d - C) S^2 \) | 4.07 | 4.67 | 5.14 | 5.63 |
| \( (C_f - C) S^2 \) | 4.01 | 4.62 | 5.04 | 5.42 |
| \( \mu_s \) | 0.60 | 0.62 | 0.65 | 0.70 |
| \( \mu_d \) | 1.70 | 1.82 | 1.96 | 2.20 |
| \( \mu_t \) | 12.82 | 15.06 | 17.80 | 23.18 |

Tables I-III summarize, in a particularly stark manner, much that is already known about the transition metal series from complete band structure calculations, for example:

1) The transition-electron bands narrow and lower along any given series [12].

2) In the d-transition series the conduction bands are predominantly narrow d-bands superimposed upon the s-p structure whereas in the 4f's the f bands are so narrow that they play no role in the band structure [8]. For example the band mass of 150 for gadolinium is some 20 times greater than that of iron. Thus in the rare earths the bands develop out of d-bands hybridizing strongly with s-p bands. How-

<table>
<thead>
<tr>
<th>5s' 4d' 5p'</th>
<th>5s' 4d' 5p'</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_s )</td>
<td>2.30</td>
</tr>
<tr>
<td>( \mu_d )</td>
<td>43.0</td>
</tr>
<tr>
<td>( \mu_t )</td>
<td>108.0</td>
</tr>
</tbody>
</table>

| \( (C_d - C) S^2 \) | 4.39 | 4.39 | 4.93 | 5.18 | 5.42 | 5.70 | 5.94 |
| \( (C_f - C) S^2 \) | 4.01 | 5.04 | 4.62 | 5.42 | 4.01 | 5.04 | 4.62 | 5.42 |
| \( \mu_s \) | 0.60 | 0.62 | 0.63 | 0.63 | 0.64 | 0.66 | 0.67 | 0.69 |
| \( \mu_d \) | 1.76 | 1.85 | 1.94 | 1.94 | 1.89 | 1.96 | 2.02 | 2.08 |
| \( \mu_t \) | 12.00 | 15.98 | 21.00 | 21.00 | 19.02 | 23.78 | 29.80 | 36.76 |

\( f s' d' \) | \( f s' d' \) | \( f s' d' \) | \( f s' d' \) | \( f s' d' \) | \( f s' d' \) | \( f s' d' \) | \( f s' d' \)
ever in the lighter actinides the masses of f-electrons are comparable with those at the latter end of the 3d transition series and may play a role in band structure and bonding as found by Freeman and Koelling [1]. Further hybridization between any two bands is proportional, approximately, to the root mean square of their bandwidths [10] which apart from relative energy placings suggests that actinide f-electrons hybridize strongly with d and s electrons. The heavier band masses for the later actinides (Am and beyond) places them in the same region as the light rare earths, therefore one does not expect them to contribute to conductivity.

3) Table III shows how the f bands narrow and rise and the d bands are raised as the lattice parameter is increased and this should be borne in mind when comparing table II with results for the exact lattice parameter of the metal.

It is a simple matter to estimate f-bandwidths from table II as has been done by Andersen [9] for d-electrons. The spread, \( \Delta S_{3f} \), of the f-structure constants at \( T \) (where \( \Delta S_{3f} \) is a maximum) is \( \approx 45 \) for the fcc structure. This canonical energy is readily reduced to the real energy by scaling with \( (1/\mu_s^2) \). Then, for uranium \( s^2d^f \), for example, the unhybridized bandwidth is 3.25 eV when \( S \) is 3.55 A.U. Anderson [9] finds the 3d structure constant spread \( \Delta S_{2f} \) (at \( X \)) to be \( \approx 28 \) which yields a bandwidth of 5.4 eV for the d-electrons of iron. The band structure contribution to the total energy, and therefore to bonding, may also be written down in the unhybridized limit.

According to Pettifor [16]

\[
U_{gs} = \sum_{\mathbf{k} \in \mathbf{B}} E^{1}_{\mathbf{k}} = N_{s} C_{s} + \mu_{s} + \cdots
\]

where \( \mu_{s} \) is the n'th canonical energy moment of the l-band which is fixed for a given structure. The bonding integral \( \mu_{s} \) is largest in magnitude for a half filled band and falls to zero for a full band. Pettifor [16] has shown that it is this integral which is responsible for the observed crystal structure trends across the transition metal series. The development of the total energy and charge in a band in terms of canonical energy moments is conceptually important and directly useful to accelerate convergence in self-consistent band calculations [3]. If the charge density is expanded analogously to (2) the first term is just the renormalized atom contribution [17] and the second yields the bonding charge density which integrates to zero over the atomic sphere.

More complete self-consistent ASA calculations for the actinides by Skriver, Andersen and Johansson [18], and Glötzel [19] (for thorium) show a significant f-contribution to bonding for the lighter actinides which is necessary to explain the equilibrium atomic volumes. The bandwidths obtained are similar to those obtained from table II and the f-occupation corresponds quite closely to those chosen in the table.

3. Features of f-bands in actinide compounds. — Earlier attempts by Kmetko and Weber [20] and Adachi and Imoto [21] to compute band structures for NaCl actinide compounds suffered from being non-relativistic and from using tight-binding methods that contained rather restrictive approximations. A more recent very sophisticated series of studies of actinide intermetallics by Koelling and Arko [22] is in progress. The most complete studies of monopnictides and monochalcogenides have been firstly made by Davis [23] and more recently by Allen and Brooks [24]. It is to these studies that we shall refer in this paper. The relativistic effects for the actinides are well documented [1], in particular the Darwin shift that brings the 7s half a Rydberg down against the 5f levels. The semi-relativistic calculations of Allen and Brooks [24] include the major corrections, mass velocity and Darwin terms, but as yet spin-orbit coupling has not been included to reduce the size of the problem. Spin-orbit coupling may not in the end be neglected, however, as has been frequently demonstrated by Freeman and Koelling [1], especially for accurate calculations with narrow f-bands where it is of the order of the crystal field splitting. In his non-relativistic KKR calculations Davis [23] used charge densities from relativistic atomic calculations arguing that this in some way incorporated relativistic effects.

The simplifying ideas of the previous section do not carry particularly well to studies of compounds. However it can be useful to discuss unhybridized l-bands, one for each component of the compound, before considering complete band calculations. Table IV shows parameter lists for uranium in uranium antimonide as a function of lattice parameter. One notices immediately that, for the case corresponding to the lattice parameter 4.8 \( \AA \), the d-bands are lowered relative to the s-bands and the f-bands are lowered relative to the d-bands compared with the metal. All band masses have decreased, but particularly the f-band mass. These effects are due to the decreased atomic sphere radius to which the broad s-bands, which are more free electron like, are not sensitive. One may expect in general a lowering of f and d electron energies relative to s-electron energies in going from metal to compound. The change of band mass is more than compensated by the change in structure constants in the compounds. In a binary compound, for spheres of equal size about each component, the structure constants are scaled by \( (1/2)^{(n+1)/2} \) and this produces a parallel scaling of the unhybridized bandwidth according to (1). Thus for USb the unhybridized f-bandwidth for a lattice parameter of 4.8 \( \AA \) would be 1.76 eV to be compared with 3.25 eV for the metal with the same lattice.
parameter. In table IV the range of lattice parameter spanned corresponds to the actinide pnictide range UN-USb and the approximate doubling of band mass corresponds to halving the bandwidth.

Table IV. — Potential parameters for uranium antimonide as a function of lattice parameter.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lattice Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$ (A.U.)</td>
<td>2.697 2.814 2.931 3.152</td>
</tr>
<tr>
<td>$(C_s-C_s)S^2$</td>
<td>-1.45 -0.92 1.10 2.34</td>
</tr>
<tr>
<td>$(C_t-C_t)S^2$</td>
<td>3.29 -1.61 -0.66 +0.49</td>
</tr>
<tr>
<td>$\mu_s$</td>
<td>0.55 0.55 0.56 0.57</td>
</tr>
<tr>
<td>$\mu_d$</td>
<td>1.26 1.39 1.44 1.60</td>
</tr>
<tr>
<td>$\mu_t$</td>
<td>7.59 8.78 10.22 13.26</td>
</tr>
</tbody>
</table>

The unhybridized bands of uranium and sulphur in US are shown in figure 1. The ordering of bands of different angular momentum ($l$) is determined by the potential parameters whereas the ordering of the bands $l_i$ ($i = 1, 2, l + 1$) for a given angular momentum is determined by the structure constants. Therefore, at $\Gamma$ before hybridization, the $\Gamma_{15}$ triplet always lies lowest and just appears at the top of the figure, with the $\Gamma_{12}$ doublet lying higher. At the bottom of the d-bands come the 5f-bands divided into a $\Gamma_{15}$ singlet, a $\Gamma_{13}$ triplet and a $\Gamma_{25}$ triplet, in ascending order. The broad uranium s-band comes next with the sulphur p-bands at the bottom. The full band structure for US in a local density approximation [14] is shown in figure 2a. The most significant change is that the complex band structure above what were sulphur p-bands lies below the unhybridized f and d-bands. The lower of these bands are occupied in the solid resulting in a net energy gain relative to the unhybridized situation. Two kinds of bonding have occurred:

1. the uranium f-electrons have hybridized strongly with d-electrons on neighbouring uranium atoms — this is why so many bands have appeared where there was only an s-band,
b) the f-d electrons have hybridized strongly with the p-electrons of the sulphur. (a) is the kind of bonding found in the actinide metals and is part of the f-contribution to their bonding. The hybridization off-diagonal in the components of the compound is also very strong. Analysis of the angular momentum projected density of states [24] shows considerable f-d character in the \( \Gamma_{15} \) valence band.

There is little charge transfer to the pnictogen and a genuine covalent bond with f-character appears to have formed leaving little or no ionicity although we must await the completion of self-consistent calculations to know the charge transfer exactly.

The strong hybridization between f-d and p-electrons is a feature of the entire uranium monopnicdite series [23, 26]. We have observed that as the pnictogen becomes heavier (and the lattice parameter increases) the complex band structure above the \( \Gamma_{15} \) valence band narrows [24]. This is the effect of reducing overlap by increasing lattice parameter and it is not surprising that neutron experiments on USb by Lander and Sinha [25] indicate magnetism that may be explained by a local moment picture. It is also easy to see how the heavy p-state admixture plays a role in producing large anisotropies. There are two triplets for f-orbitals in a cubic structure one with prolate (p-like) and one with oblate charge density. It is the oblate \( \Gamma_{15} \) f-states that can be trapped in planes with moments pointing perpendicular to the planes since their charge densities point along the cubic axes, overlapping the pnictogen p-states.

Finally, in figure 2b is shown the US band structure in the Slater exchange approximation [13] \( \chi_a = 1 \). Clearly the exchange approximation makes significant changes to the band structure but it is local density approximations [4, 14, 15] that are believed to yield the best results for the actinides where the statistical approximation should hold. Figure 2c shows the band structure of europium sulphide computed under the same conditions as the uranium sulphide in figure 2b. The entirely different character of f-electrons in EuS is evident from the diagram and requires no further comment.

4. Conclusion. — A simple demonstration of the participation of f-electrons in bonding has been attempted. Although unhybridized band theory in ASA is a simplification, a comparison of unhybridized bands and a full band structure isolates the roles played by direct f-f overlap and f-d-p hybridization in actinide compounds. ASA may be a poor approximation when applied to compounds, with a rather more open structure than metals, but any errors are small when set against the magnitude of the effects described here. It should also be noted that the neglect of spin-orbit coupling is most serious for the actinide 6p states for which it is of the order of half a Rydberg, and that the 6p's play a role in bonding. In fact the upper spin-orbit split 6p-band may overlap the 3p-band of a pnictogen or chalcogen [26].

In band theories the Coulomb correlation integral

\[
U = \int \psi_{nk}^*(r) \psi_{nk}(r) (e^2/r_{ij}) \times \psi_{nk}^*(r) \psi_{nk}(r) \, dr_1 \, dr_2 \tag{3}
\]

where here, \( nk \) labels the narrow f-bands, is not neglected but is replaced by a local effective potential [4]. If the wave function \( \psi_{nk} \) is large in only a small region (as is the case for narrow bands) this approximation becomes poor leading to a Mott-Hubbard transition [27] for the electrons in question, primarily due to intra-site terms in (3).

Equation (3) is written with the bare Coulomb interaction \( (e^2/r_{ij}) \). In a band theory aimed at computing ground state properties \( U \) may be replaced by an effective screened potential \( U_{\text{eff}} \) [28] which is rather smaller than \( U \). The variety of estimates of \( U_{\text{eff}} \) is enormous (see e.g. the review by Edwards [29]). However, without the benefit of s-electron shielding or, in an actinide, s-d shielding, it would be larger than the f-bandwidths found in all actinide compounds. An interesting contrast is between the light actinide dioxides (fluorite structure) which are not metallic and the light actinide pnictides which are. In the oxides the electronegativity of oxygen produces an ionic compound (although probably not an \( A^{4+} \) ion) [30, 31]. This is sufficient, not only to fill the oxygen p-bands but to draw the actinide 5f level below the actinide 7s, 6d bands which are left empty. Without the benefit of s-d shielding the 5f bands have no Fermi surface and there is an integral number of f-electrons [33] although the lattice parameter of UO3, for example, is not especially large. A similar situation exists for 3d-monoxides with the Rocksalt structure [32].

Acknowledgments. — The author is grateful to O. K. Andersen for much advice concerning LMTO's since the beginning of this research and to H. L. Skriver for helping to solve some of the initial problems. Conversations with G. H. Lander stimulated much of the work on NaCl compounds. Many discussions with R. Allen, who also made the band structure of EuS shown in figure 2 are also gratefully acknowledged.
References

[26] Freeman, A. J., in Rare Earths and Actinides 1977, Inst. of Phys. Conf. series no. 37, W. D. Corner and B. K. Tanner, eds. (Inst. of Physics, Bristol and London) 1978, p. 120.
DISCUSSION

Pr. B. R. Cooper. — Have you projected out localized density of states so that you can look at effective $f$ electron valence variation with lattice parameter for the uranium pnictides?

M. S. S. Brooks. — We have been working on projected densities of states for this purpose and to start self-consistent calculations. We have some results but are not happy enough with the programs to say what they are yet—perhaps in a few months.

Dr. G. Solt. — I have two questions:
1) Have you tried to calculate the total energy of the actinides by your formalism? By doing this you could have determined the actual lattice spacing and compare it with the observed one.
2) You have got impressively big effective masses for the $f$ band for quite a few metals. What is your feeling, at what stage your assumption that there are well defined occupancies for the calculated Bloch states becomes no more valid?

M. S. S. Brooks. — You are talking essentially of self-consistent calculations and that is exactly what we are now working on. It will take a little time. However, for the actinides, there are now available such calculations by Koelling (APW) and Skriver et al. (MTO), and Blötzell (MTO), which appear in the reference list of this paper.

Pr. J. Grunzweig-Genossar. — There are several groups calculating electron band structures using different approximations. I would like to see a comparison or a review of these results.

M. S. S. Brooks. — This is a big question. All the band structure methods (APW, KKR, MTO, etc.) should give the same results for the same potential if carried to convergence. We constructed a potential for fcc thorium metal following exactly the prescription of Koelling and Freeman in their calculation of some years ago. It was gratifying to find that we obtained exactly the same results as far as we could see. However with the atomic sphere approximation (spherical symmetry) we would expect to lose a bit in accuracy to Koelling’s non-spherical calculations. Secondly self-consistent calculations should always be more accurate especially since the potential formalism is then well defined.

In addition there are the cluster theories which will normally produce different results since the physical approximations are different. I suspect they should be better for localized electrons but can’t prove it. However the similarity between our $\text{UO}_2$ results (MTO’s) and Ellis’s molecular cluster calculation results (both in this conference) is remarkable. Keller’s cluster calculations for UN (this conference) seem also to produce quite similar results to ours.

Dr. J. Gal. — Could your calculations predict a first order magnetic transition in $\text{UO}_2$?

M. S. S. Brooks. — No — certainly not. The first order transition in $\text{UO}_2$ is discussed in papers by Lander, Faber, Freeman, and Desclaux (Ref. [33] in reference list) and is associated with quadrupolar ordering (Jahn-Teller) in a local moment picture. The original theory of this transition may be found in papers by Allen some years ago.

Comment by Dr. Lander. — I think we should finally recognize that Blume’s theory for $\text{UO}_2$ is wrong. The theory is an elegant one, but the ground state of $\text{UO}_2$ is a $T_2$ triplet. That is now established experimentally beyond all doubt.

Dr. Schoenies. — What is the effective mass for the $6d$-band in $\text{USb}$?

M. S. S. Brooks. — I don’t have the mass parameter for the compounds with me but can always send them to you. In any case please note that the band masses that we refer to are defined in the papers of O. K. Anderson (reference list at the end of the paper) and may not correspond to band masses that you have in mind although they should be related.