UvA-DARE (Digital Academic Repository)

Simple calculations of hybridization effects in UTX and U2T2X compounds

Prokes, K.; Brück, E.H.; Nakotte, H.; de Chatel, P.F.; de Boer, F.R.

DOI

[10.1016/0921-4526\(94\)00351-U](https://doi.org/10.1016/0921-4526(94)00351-U)

Publication date

1995

Published in

Physica B-Condensed Matter

[Link to publication](#)

Citation for published version (APA):

Prokes, K., Brück, E. H., Nakotte, H., de Chatel, P. F., & de Boer, F. R. (1995). Simple calculations of hybridization effects in UTX and U2T2X compounds. *Physica B-Condensed Matter*, 206-207, 8-10. [https://doi.org/10.1016/0921-4526\(94\)00351-U](https://doi.org/10.1016/0921-4526(94)00351-U)

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Simple calculation of hybridization effects in UTX and U_2T_2X compounds

K. Prokeš*, E. Brück, H. Nakotte, P.F. de Châtel, F.R. de Boer

Van der Waals–Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

Abstract

The band widths of several UTX and U_2T_2X compounds (T: transition metal, X: p-metal) are evaluated by means of a tight-binding method. The magnetism in both groups of compounds is governed by the hybridization between U f-states and transition-metal d-states. Comparing the sum of all hybridization effects, we find approximately the same hybridization effects in both groups of compounds. We also observe a decrease of the band width with increasing atomic number Z within a transition-metal series. By comparing the band width with the theoretical critical energies for the f^3 and f^2 configurations, it is in some cases possible to predict whether the ground state is magnetically ordered or not.

A rather accurate description of the ground-state properties of a particular uranium compound can be achieved by means of the local-density approximation (LDA) method. The results obtained by means of the LDA method have been found to agree in most cases with experimental findings [1]. However, this method is rather time consuming and requires considerable computation effort. For certain considerations a faster procedure may be preferable, even if it is less accurate.

The aim of this paper is to present results obtained with a simple tight-binding type of calculation applied to two groups of U compounds by which it is possible to get a qualitative and in some cases also a quantitative estimate of the importance of hybridization effects in the formation of the uranium magnetic moments. This method was initially used to calculate the d-band electronic structure of compounds [2] and later adapted to determine the interaction between s, p, d and f atomic orbitals [3–6].

In order to describe trends in magnetic properties within certain group of compounds, one has to calcu-

late the mixing of the states for a two-centre bond accounting for all contributions. The model that we apply is in fact a combination of Anderson's LMTO theory [7] and the transition-metal pseudo-potential theory [8] and gives as a result the second moment of the f-hybridized band:

$$\langle (E_k - \varepsilon_f)^2 \rangle = \sum_i \frac{n_i}{2l' + 1} \times (V_{ll'\sigma}^2 + 2V_{ll'\pi}^2 + 2V_{ll'\delta}^2 + 2V_{ll'\varphi}^2) \quad (1)$$

where

$$V_{ll'm} = (\eta_{ll'm} \hbar^2 / m_e) \left[\sqrt{(r_i^{2l-1} r_{i'}^{2l'-1})} / d^{l+l'+1} \right] \quad (2)$$

denotes a general hybridization element between two ions with radii r and r' at distance d . The indexes are the angular moments l, l' ($l = 0, 1, 2, 3$ for s, p, d and f orbitals) and the symmetry of the bond m ($m = 0, 1, 2, 3$ for $\sigma, \pi, \delta, \varphi$ bonds). The electron mass is denoted by m_e and $\eta_{ll'm}$ are general coefficients which have been derived by Wills and Harrison [9] and tabulated by Brück [11]. The n_i in Eq. (1) denote the number of nearest neighbours with orbital quantum number l' . Since the individual matrix elements are additive, a higher coordination number increases the total hybridization and thus one should

* Corresponding author.

concentrate on groups of isostructural compounds. The second moment derived may be compared with the criterion for localization of the magnetic moments due to the Coulomb repulsion U [7] to give an idea about the tendency towards magnetic ordering. If the covalent energy (square root of the total hybridization energy) is smaller than $U\sin^2(Z_f/14)$, with Z_f the number of f electrons, localization and thus magnetic ordering can be expected. For U compounds, the critical energy equals 1.38 and 0.68 eV for the f^3 and f^2 configurations, respectively.

The atomic radii of the respective ions have been tabulated in Refs. [4] and [6] and the only experimental data necessary are the distances between the ions together with the coordination numbers or, equivalently, the atomic positions in the structure.

We have applied the above described calculation on two groups of U compounds: U_2T_2X and UTX . The first group of compounds studied crystallizes in the tetragonal U_3Si_2 type of structure. In this structure each U atom has seven U neighbours (five within the plane and two along the c axis). Furthermore, each U atom has six transition-metal neighbours and finally, there are four p -metal neighbours for each U atom. In this case, the distances were taken from Ref. [10] and the results of the calculations are listed in Table 1.

The second group of compounds crystallizes in the hexagonal $ZrNiAl$ structure in which each U atom has four U nearest neighbours within the basal plane at a distance of about 350 pm and two next nearest U neighbours at a distance equal to the lattice constant c . There are two in-plane d -metal neighbours, four out-of-plane d -metal neighbours and finally six out-of-

plane p -metal neighbours. The atomic positions were taken partly from neutron-diffraction results and partly from Ref. [11]. The results of the calculations are summarized in Table 2.

Inspecting the values in Tables 1 and 2, we find that the magnetism in these two groups of compounds is governed by the f - d and f - p hybridization, as the values for V_{ff} are considerably smaller. We observe a decrease of the covalent energy with increasing Z within the transition-metal series in both groups of compounds (e.g. from Co to Ni), which implies an increasing likelihood of magnetic ordering in this direction.

As already mentioned above, a non-magnetic ground state can be expected if the covalent energy is larger than the critical energy equal to 1.38 and 0.68 eV for the f^3 and f^2 configurations, respectively. This critical energy depends on the average f -electron occupancy of U . As the calculated covalent energy for U_2Ir_2Sn is larger than 1.38 eV, we may expect this compound to be non-magnetic, which is indeed found experimentally. Additionally, an f count only slightly smaller than 3 also implies a non-magnetic ground state for U_2Rh_2In . As the reduction of the f count is known to be the strongest in compounds containing 3d metals, also the non-magnetic states of U_2Co_2In and U_2Co_2Sn do not surprise. LDA calculations [12] have indeed shown that the average f -occupation in U_2Co_2In is even less than 2.0 which means that the critical energy is lower than 0.68 eV. On the other hand, for both Ni - and both Pd -containing compounds rather low values for the covalent energy are found,

Table 1

Hybridization energy of U_2T_2X compounds. V_{ff} denotes the different types of contributions. In the last column, the sum over all contributions is given. The asterisk denotes the presence of magnetic ordering

Compound	V_{ff} (meV)	V_{fd} (meV)	V_{fp} (meV)	Total (eV)
U_2Co_2In	257.6	936.7	709.7	1.203
U_2Ni_2In	216.3	773.4	667.1	1.044*
U_2Rh_2In	195.0	1144.2	603.7	1.308
U_2Pd_2In	160.7	920.3	549.4	1.038*
U_2Pt_2In	164.2	1076.1	550.1	1.220
U_2Co_2Sn	242.7	923.1	689.5	1.177
U_2Ni_2Sn	208.8	750.8	646.9	1.012*
U_2Rh_2Sn	189.2	1140.2	587.1	1.296*
U_2Pd_2Sn	158.3	914.7	532.3	1.070*
U_2Ir_2Sn	191.8	1292.5	582.0	1.430
U_2Pt_2Sn	166.8	1087.1	533.2	1.222*

Table 2

Hybridization energy of UTX compounds. V_{ff} denotes the different types of contributions. In the last column, the sum over all contributions is given. The asterisk denotes the presence of magnetic ordering

Compound	V_{ff} (meV)	V_{fd} (meV)	V_{fp} (meV)	Total (eV)
$UFeAl$	272.3	825.8	823.6	1.197
$UCoAl$	268.4	755.7	824.9	1.150
$UNiAl$	254.4	647.8	780.4	1.046*
$URuAl$	223.5	1079	732.2	1.323
$URhAl$	201.4	945.3	706.2	1.197*
$UFeGa$	264.4	843.9	872.2	1.242
$UCoGa$	274.6	783.1	884.0	1.212*
$UNiGa$	266.1	667.4	843.2	1.107*
$URuGa$	197.3	109.5	776.7	1.357
$URhGa$	200.7	967.3	752.4	1.241*
$UIrGa$	196.1	1082	743.9	1.328*
$UPtGa$	186.2	937.4	691.8	1.179*

which is consistent with the observation of magnetic order. Finally, we cannot conclude about the ground state of $\text{U}_2\text{Pt}_2\text{In}$, $\text{U}_2\text{Rh}_2\text{Sn}$ and $\text{U}_2\text{Pt}_2\text{Sn}$ on the basis of a tight-binding calculation only, but the experimentally observed magnetic ground state of the latter two compounds suggests that they have an f count close to 3. For these compounds, more sophisticated band-structure calculations have to be performed.

Inspecting the values listed in Table 2 we see that none of the UTX compounds investigated exceeds the limit of 1.38 eV for localization of the f^3 configuration. However not all compounds exhibit magnetic order. In the original papers [4,6] is mentioned that the hybridization energies calculated in the above-mentioned scheme are underestimated for compounds containing 3d elements and overestimated for compounds with 5d elements. This statement is supported by the same value of the hybridization energies obtained for UFeAl which is non-magnetic (or by the even lower value found for non-magnetic UCoAl) and URhAl which exhibits magnetic order. On the other hand, both Ru-containing compounds are non-magnetic although in both cases the hybridization energies are lower than 1.38 eV. This points to the fact that the average f -electron occupancy is lower than 3 in these compounds.

For UNiAl we have found the hybridization energy to be 1.046 eV and for UCoGa 1.212 eV. Both compounds exhibit magnetic order. This means that the critical energy for magnetic ordering is shifted towards lower values in the case of Al-containing compounds. For UIrGa , which is magnetically ordered at low temperatures, we find a covalent energy close to the value expected for the f^3 configuration.

Acknowledgement

This work is part of the research program of the ‘Stichting voor Fundamenteel Onderzoek der Materie’ (FOM), which is financially supported by the ‘Nederlandse Organisatie voor Wetenschappelijk Onderzoek’ (NWO).

References

- [1] O. Erriksson, B. Johansson, R.C. Albers, A.M. Boring, and M.S.S. Brooks, *Phys. Rev. B* 42 (1990) 2707.
- [2] W.A. Harrison and S. Froyen, *Phys. Rev. B* 21 (1980) 3214.
- [3] W.A. Harrison, *Phys. Rev. B* 28 (1983) 550.
- [4] G.K. Straub and W.A. Harrison, *Phys. Rev. B* 31 (1985) 7668.
- [5] D.D. Koeling, B.D. Dunlap and G.W. Crabtree, *Phys. Rev. B* 31 (1985) 4966.
- [6] W.A. Harrison and G.K. Straub, *Phys. Rev. B* 36 (1987) 2695.
- [7] O.K. Anderson, *Phys. Rev. B* 12 (1975) 3060.
- [8] W.A. Harrison, *Phys. Rev.* 181 (1969) 1036.
- [9] J.M. Wills and W.A. Harrison, *Phys. Rev. B* 28 (1983) 4363.
- [10] M.N. Peron, Y. Kergadallan, J. Rebizant, D. Meyer, J.M. Winand, S. Zwirner, L. Havela, H. Nakotte, J.C. Spirlet, G.M. Kalvius, E. Collineau, J.L. Oddou, C. Jeandey and J.P. Sanchez, *J. Alloys Comp.* 201 (1993) 203.
- [11] E. Brück, PhD Thesis, University of Amsterdam (1991).
- [12] M. Diviš, M. Richter and H. Eschrig, *Solid State Commun.* 90 (1994) 99.