

HYBRIDIZATION EFFECTS IN SOME UX_5 COMPOUNDS

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Abstract. The presence of the magnetic moments on the uranium atoms in some of the $UX_{5-x}Y_x$ compounds (X and Y are 3d, 4d or 5d transition element) is discussed using the hybridization strength of the s , p , d and f atomic orbitals. By using a semi quantitative band structure approach due to Straub and Harrison, the hybridization effects in these binary and ternary series of isostructural compounds were evaluated. Comparing the bandwidth with a theoretical critical energy (for f^2 and f^3) in order to predict if the ground state is magnetically ordered it seems that f^3 is not the exact electronic configuration for uranium in this class. This fact is correlated with the suggestion that the U valence in the UCu_5 group is a mixture of values where the tetravalent component (f^2 configuration) is a significant one.

Key words: Uranium UX_5 compounds, hybridization effects, Uranium magnetic moment existence.

1. INTRODUCTION

The binary and ternary uranium compounds of $UX_{5-x}Y_x$ type (X and Y are 3d, 4d or 5d element) structurally and magnetically investigated show inside a group similar structural symmetry (cubic of $AuBe_5$ type) and close lattice parameters, but a large variety of magnetic properties [1]. The uranium 5f electrons mainly determine the magnetic behavior of these compounds. The contribution of the other components to the magnetic moment is not important, but they influence the magnetic properties by modifying the state of the uranium 5f electrons. If the magnetic moments exist in these compounds, they are positioned only on the uranium atoms and not on the transition metals. The main mechanism considered for the delocalization of uranium 5f electrons is the hybridization. The influence of the hybridization effects in the uranium magnetic moment formation is appreciated using the Straub and Harrison method for calculation of the interactions between s , p , d and f atomic orbitals [2,3,4].

The present study intends to evaluate the f , d hybridization strength V_{II} , covalent energy V_{total} and to discuss the magnetic properties of the UX_5 group of binary and ternary compounds according to the criterion of the magnetic ground state.

2. HYBRIDIZATION EFFECTS

The ff , fd and fp hybridization is the mechanism of the delocalization of f electrons and is the essential factor in determining the magnetic ordering presence in uranium intermetallics [5, 6, 7]. The method developed by Straub and Harrison which estimates the hybridization strength is to calculate the interactions between s , p , d and f atomic orbitals. The used model is based on the linear muffin-tin orbitals (LMTO) theory and the transition metal pseudopotential formalism. The two-center couplings between f orbitals of uranium and s , p , d orbitals of neighboring elements are calculated accounting for all contributions. The general hybridization matrix elements are:

$$V_{ll'm} = (\eta_{ll'm} \hbar^2 / m_e) [(r_i^{2l-1} r_i'^{2l'-1})^{1/2} / d^{l+l'+1}].$$

The included parameters are the atomic radii of the interacting atoms r_i and r_i' , the distance d between these atoms, the angular momenta l and l' ($l, l' = 0, 1, 2$ and 3 for s, p, d and f orbitals). The index m describes the symmetry of the bond ($m = 0, 1, 2$ and 3 for σ, π, δ and φ bonds respectively) and m_e represents the electron mass. The coefficient $\eta_{ll'm}$ was obtained from:

$$\eta_{ll'm} = \frac{(-1)^{l'+1}}{6\pi} \frac{(l+l')!(2l)!(2l')!}{2^{l+l'} l! l'!} \times (-1)^m \left(\frac{(2l+1)(2l'+1)}{(l+m)!(l-m)!(l'+m)!(l'-m)!} \right)^{1/2}.$$

The strength of the total fl' hybridization is evaluated according to

$$V_{fl'} = \left[\sum \frac{n_i}{2l'+1} (V_{fl'\sigma}^2 + 2V_{fl'\pi}^2 + 2V_{fl'\delta}^2 + 2V_{fl'\varphi}^2) \right]^{1/2}$$

where n_i is the number of neighbors having angular momentum l' at a distance d .

The second moment of the f -hybridized band

$$\langle (E_F - \varepsilon_f)^2 \rangle = V_{total}^2 = V_{ff}^2 + V_{fd}^2 + V_{fp}^2$$

may measure the tendency of the delocalization of f electrons [4] and V_{total} is considered as the total covalent energy [6]. ε_f represents the location of the f level relative to the E_F -Fermi energy. The criterion for a localized magnetic moment on uranium ion considers that V_{total} must be inferior to the critical energy

$$U \sin^2 \left(\frac{Z_f \pi}{14} \right),$$

where U is the Coulomb repulsion (3.56 eV for uranium) and Z_f represents the number of f electrons [4]. An intermetallic compound is expected to have magnetic moment if V_{total} is smaller than the critical energy. This critical energy depends on the average occupancy of uranium f electron and is 1.38 eV and 0.68 eV for f^3 and f^2 configurations respectively [4].

3. RESULTS

The values for the hybridization energy are dependent on the interatomic distance between uranium and the others d atoms and on the d electrons number; the V_{ff} value is dependent on the interatomic distances and the atomic radii are dependent on the number of d electrons. The atomic radii for uranium and d atoms were taken from [4]. The atomic positions were taken from [8].

The number of nearest neighbors is specific to the symmetry type. For investigated class of UX_5 compounds the crystalline symmetry is of the $AuBe_5$ type. In this cubic structure, 12 uranium neighbors surround uranium atoms. The $X(Be)$ positions have two crystallographically inequivalent sites characterized by large tetrahedral ($4c$) with a cubic symmetry and small tetrahedrons ($16e$) with a trigonal symmetry around $[111]$ axis. The uranium atom has 4 X neighbors at $4c$ sites and 12 X neighbors at $16e$ sites. In $UX_{5-x}Y_x$ compounds the $4c$ sites are occupied by the atoms having larger atomic radii; in UCu_4Ag and UCu_4Au , Ag and Au atoms occupy preferentially $4c$ positions. They contribute to the stability of long-range magnetic order. An antiferromagnetic ordering is established in both compounds, with transition temperatures higher than that of UCu_5 [9, 10]. The diluents $Y=Ni$ and Pd have a rather destructive effect on the magnetic order. UCu_4Pd presents a Curie Weiss type of paramagnetism. The same behavior is followed for further Pd substitution up to UCu_3Pd_2 .

The calculated V_{ff} and V_{total} values for UX_5 and $UX_{1-x}Y_x$ compounds are listed in the Table 1. The last column presents the type of magnetic behavior, the transition temperature for ordered compounds and the references we used.

Table 1

The $f-f$ (V_{ff}), $f-d$ (V_{fd}), $f-p$ (V_{fp}) hybridization and the covalent energy (V_{total}) in ternary uranium UX_5 type compounds. AF represents antiferromagnets, TDP-temperature dependent paramagnets and TIP-temperature independent paramagnets

Compound	V_{ff} [meV]	V_{fd} [meV]	V_{total} [meV]	T [K] Refs.
UNi_5	53.3	1226	1227	TIP [1]
UCu_5	42.4	924	925	AF, 15K [1]
UPt_5	28.5	1283	1283	TDP [1]
UCu_4Ni	44.1	987	988	TDP [1]

Table 1 (continued)

UCu ₄ Pd	40.5	1486	1486	TDP[1]
UCu ₄ Ag	39	963	964	AF,18K[1]
UCu ₄ Au	38	1011	1011	AF,27K[1]
UPt ₄ Pd	53	1218	1219	TIP[1]
UPt ₄ Ir	30	1339	1339	TIP[1]
UPt ₄ Au	48	1076	1077	TDP[1]
UNi ₄ Au	47	1268	1269	TIP[1]
UCu ₃ Ni ₂	48	1076	1077	TDP[1]
UCu ₃ Pd ₂	37.4	1082	1083	TDP[1]
UCu ₃ Au ₂	33	916	916	AF,13K[1]
UPt ₃ Au ₂	26	1153	1153	TDP[1]
UNi ₃ Au ₂	37	1194	1194	TDP[1]
UCu ₂ Ni ₃	49	1126	1127	TIP[1]
UCu ₂ Au ₃	29	1040	1040	TDP[1]
UNi ₂ Au ₃	31	1129	1129	TDP[1]
UPt ₂ Au ₃	26	1148	1148	AF,4K[1]
UCuNi ₄	53	1218	1219	TIP[1]
UCu _{2.5} Ni _{2.5}	48	1093	1094	TDP[13]
UCu _{4.5} Ni _{0.5}	43	954	955	AF,5K
UAuNi ₄	47	1268	1269	TIP[1]

4. DISCUSSION

The discussion of V_{ff} values is valid inside a series of the isostructural compounds. For UX₅ compounds the direct mutual overlap of $5f$ orbitals of uranium has very low values, V_{ff} being only about 4 % from V_{total} , and decreases inside a group as the atomic number Z becomes higher. This observation is valid for all studied groups UX₅, UX₄Y, UX₃Y₂, UX₂Y₃ and UXY₄. Low V_{ff} value is a statement analogous to the Hill criterion, which assumes that the U-U interatomic distances superior to 3.5 Å lead to f electron localization. In these classes of uranium compounds, the U-U distances are about 5 Å and shows such low f - f hybridization.

The fd hybridization is the dominant process for the strong delocalization of f electrons. The U-X(Y) distances are about 3 Å; the U neighbors positioned at $4c$ sites have distances with $\approx 6\%$ superior to those situated in $16c$ sites. Intense V_{fd} values observed in the great majority of the UX₅ type compounds leads to the paramagnetic type behavior and the absence of the magnetic moment on uranium atoms. The lowest magnitudes for V_{fd} are characteristic to ordered compounds, where uranium moments are antiferromagnetically oriented.

Intense V_{fd} values seem to influence the temperature of the ordering state disappearance. Increased V_{fd} values are correlated to lower transition temperatures

[5]. The Intense V_{fd} values seem to influence the temperature of the ordering state disappearance. Increased V_{fd} values are correlated to lower transition temperatures [5]. The opposite variation of the magnetic transition temperature and V_{fd} as functions of composition for different systems $UCu_{5-x}Au_x$ and $UCu_{5-x}Ni_x$ is observed (Fig. 1 and Fig. 2).

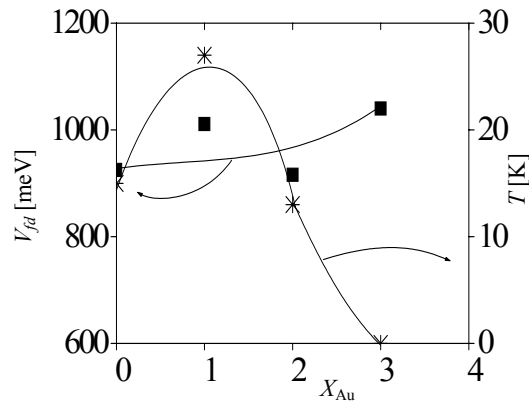


Fig. 1 – The x_{Au} dependence of V_{fd} and the transition temperature for $UCu_{5-x}Au_x$ systems.

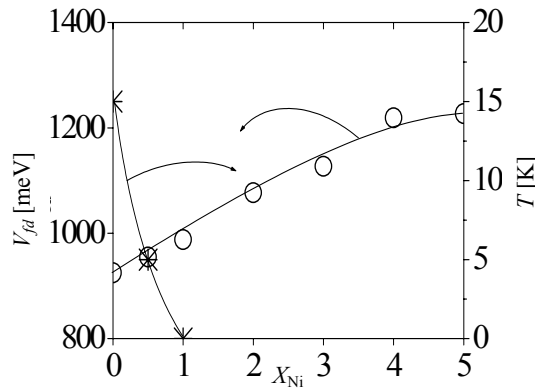


Fig. 2 – The x_{Ni} dependence of V_{fd} and the transition temperature for $UCu_{5-x}Ni_x$ systems.

The delocalization tendency of f electrons was measured comparing the critical energy for $5f^2$ and $5f^3$ configurations (0.68 eV and 1.38 eV respectively) with the covalent energy values. The unordered compounds present a V_{total} inferior to 1.38 eV. For this class of compounds this limit of 1.38 eV seems to judge incorrect the magnetic uranium moment existence. This fact leads to the conclusion that $5f^3$

electron occupancy of uranium is not the proper electronic configuration for UX_5 class. This may be connected to the suggestion that in UCu_5 group of compounds the U valence is a mixture of values [11]. It is assuming that the significant one is the tetravalent component ($5f^2$ configuration) and in such situation, the critical energy is lower. Comparing these results with similar ones [7,12] performed on other classes of U compounds, the U-U hybridization has very low values and the dominant influence on the magnetic moment formation on U sites is the $f-d$ hybridization.

5. CONCLUSIONS

The results of the hybridization effects evaluated in the frame of Straub and Harrison method show that magnetic behavior of these ternary uranium intermetallics are influenced by the hybridization. The changes in the magnetic behavior inside a $n-d$ series is determined by the fd orbitals overlap and the criterion for magnetic moment existence on U positions indicates a mixture of valences for uranium, both configurations f^2 and f^3 being present.

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