MAGNETIC BEHAVIOUR OF U(Ni$_x$Si$_{1-x}$)$_2$ SYSTEM

I. LUPTSA$^1$, M. VALEANU$^2$

$^1$Technical University, 3400 Cluj-Napoca, Romania
$^2$National Institute of Materials Physics, Bucharest-Magurele, Romania

Abstract. The magnetic measurements on U(Ni$_x$Si$_{1-x}$)$_2$ systems in the 4-500 K temperature range and fields up to 80 kOe were carried out. By increasing the nickel content, different types of magnetic ordering were evidenced: spin fluctuations for $x = 0$, spin glass state for $x = 0.25$, antiferromagnetism for $x = 0.5$ and ferromagnetism for $x = 1$. The magnetic behaviour changes are correlated to the hybridization of f-d, p orbitals.

Key words: uranium ternary compound, magnetization, hybridization effects

1. INTRODUCTION

The ternary uranium compounds U$_2$TSi$_3$, UTSi and U$_2$T$_3$Si where T is a 3d, 4d or 5d element present a large variety of magnetic properties. Inside a group the compounds show similar structural symmetry and close lattice parameters. The magnetic behavior of these compounds is mainly governed by the uranium 5f electrons. The T elements influence the magnetic properties by modifying the electronic states of uranium. The main mechanism for delocalization of uranium 5f electrons is the hybridization. An estimation of the hybridization effects in the uranium magnetic moment formation is obtained using the Straub and Harrison [11] method by taking into account interactions between s,p,d and f atomic orbitals.

In the present study we discuss the magnetic properties of the U(Ni$_x$Si$_{1-x}$)$_2$ system (U$_2$NiSi$_3$ and UNiSi for $x = 0.25$ and 0.5 ) in the Straub and Harrison formalism.

2. EXPERIMENTAL DATA

The polycrystalline samples were prepared melting the constituents in an argon arc furnace. Several times melting assured a good homogeneity. The thermal treatment at 1000 K lasted one week.

The X ray analysis indicated different types of structure as it is shown in Table 1. The lattice parameters are close to those reported for U$_2$NiSi$_3$ [1] and UNiSi [2,3]. Using the atomic positions [1,3] the nearest neighbors distances were determined.
The magnetic measurements were carried out in the 4-600 K range and fields up to 80 kOe. The accurate susceptibility values were obtained using the Honda-Owen rule: \( \chi_{\text{corr}} = \chi + cM_sH^\epsilon \). \( \chi \) correct values are obtained for \( H^\epsilon \to 0 \) in the \( \chi = f(H^\epsilon) \) representation. By this method, any possible magnetic influence of the impurity having \( c \) concentration and \( M_s \), saturation magnetization is avoided.

3. RESULTS

The compound U₂NiSi₃ is magnetically ordered below \( T_c = 25 \text{ K} \) with a magnetic moment on U atom of \( 0.6 \mu_B \). In the paramagnetic region a modified Curie-Weiss law: \( \chi = \chi_0 + C/(\theta - \theta) \) is followed [1]. The paramagnetic Curie temperature \( \theta \) and the effective magnetic moment are presented in the Table 1.

<table>
<thead>
<tr>
<th>x</th>
<th>( T_c ) (K)</th>
<th>( \mu_0(\mu_B) )/Uatom</th>
<th>( \theta ) (K)</th>
<th>( \mu_\text{eff}(\mu_B) )/Uatom</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.25</td>
<td>80(AF)</td>
<td>0.05</td>
<td>-13</td>
<td>2.1</td>
</tr>
<tr>
<td>0.75</td>
<td>20(AF)</td>
<td>0.0015</td>
<td>-425</td>
<td>2.22</td>
</tr>
<tr>
<td>1</td>
<td>25(F)</td>
<td>0.07</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

In U₂NiSi₃ the spin glass characteristics are reported [4]. The UNiSi compound was reported to undergo two antiferromagnetic transitions at 80 K and 7.5 K [5]. The thermal dependence of the reciprocal susceptibility obeys the modified Curie-Weiss law. The thermal variation of the reciprocal susceptibility of U(Ni₀.₇₅Si₀.₂₅)₂ system indicates an antiferromagnetic behavior (Fig.1).

![Fig.1 - The thermal variation of 1/\( \chi \) values for U(Ni₀.₇₅Si₀.₂₅)₂ system](image-url)
Magnetic behaviour of U(Ni$_{0.75}$Si$_{0.25}$)$_2$ system

A Curie-Weiss law describes the magnetic behaviour over transition temperature. At 4.2 K (Fig.2), the magnetization varies linearly with the field and exhibits a low nonzero value for the extrapolated magnetization M(0). USi$_2$ exhibits a spin fluctuations type behavior[6]. UNi$_2$ is a weak ferromagnet having in the paramagnetic range a temperature independent susceptibility as a dominant term [7,8]. The parameters which characterize the magnetic behaviour are summarized in the Table 1. There are indicated the references we used to compare our results.

3. HYBRIDIZATION EFFECTS

The f-f, f-d and f-p hybridization is the mechanism of the delocalization of f electrons and is the essential factor in determining the magnetic ordering in many cerium and uranium intermetallics [9]. An estimation of the hybridization intensity may be obtained using the method suggested by Straub and Harrison [10-12] to calculate the interactions between s, p, d and f atomic orbitals. The method evaluates the formation of the magnetic moments in a isostructural group of compounds calculating the two –center couplings between atomic orbitals of s, p, d, f symmetry. The hybridization matrix elements are:

$$V_{m,n} = (\eta_{m,n} \frac{\hbar^2}{m_e}) (r_r^{2r-1} r_r^{2r-1})^{1/2} / d^{l+l'+1}$$  \hspace{1cm} (1)

with:

$$\eta_{m,n} = \frac{(-1)^{l+l'} (l+l')! (2l)! (2l')!}{2^{l+l'} l! l'!} \times (-1)^{m} \left( \frac{(2l+1)(2l'+1)}{(l+m)! (l-m)! (l'+m)! (l'-m)!} \right)^{1/2}$$  \hspace{1cm} (2)

The parameters included are the atomic radii of the interacting atoms $r_i$ and $r_j$, 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). \(m\) describes the symmetry of the bond (\(m=0,1,2\) and 3 for \(\sigma, \pi, \delta\) and \(\varphi\) bonds respectively). \(m\) in Eq.[1] represents the electron mass.

According to [13] the strength of the total \(f'\) hybridization is obtained from:
\[
V_{f'} = \left[ \sum \frac{n_i}{2l'+1} \left( V_{\tilde{\sigma}}^2 + 2V_{\tilde{\pi}}^2 + 2V_{\tilde{\delta}}^2 + 2V_{\tilde{\varphi}}^2 \right) \right]^{1/2},
\]
where \(n_i\) is the number of neighbors having angular momentum \(l'\) having the distance \(d\). The second moment [11] of the hybridization band is
\[
\left( (E_F - \varepsilon_f) \right)^2 = V_{\text{total}}^2 = V_{j'}^2 + V_{jd}^2 + V_{fp}^2
\]
and indicates the delocalization tendency of \(f\) electrons and \(V_{\text{total}}\) is considered the total covalent energy. \(\varepsilon_f\) represents the location of the \(f\) level relative to the Fermi energy. The criterion for localized magnetic moment considers the \(V_{\text{total}}\) inferior to the critical energy \(U \sin^2(Z\pi/14)\) the compound is expected to have magnetic moments [11]. \(U\) is Coulomb repulsion (3.56 eV for uranium) and \(Z\) represents the number of \(f\) electrons. This critical energy depends on the average of \(f\) electron occupancy of uranium and is 1.38 eV and 0.68 eV for \(f^2\) and \(f^3\) configurations respectively [12]. The hybridization and covalent energy \(V_{\text{ff}}\) and \(V_{\text{total}}\) for the studied compounds are presented in Table 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(V_{\text{ff}}) (meV)</th>
<th>(V_{fd}) (meV)</th>
<th>(V_{fp}) (meV)</th>
<th>(V_{\text{total}}) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USi_2</td>
<td>153</td>
<td>—</td>
<td>1478</td>
<td>1486</td>
</tr>
<tr>
<td>U_2FeSi_3</td>
<td>153</td>
<td>436</td>
<td>1279</td>
<td>1360</td>
</tr>
<tr>
<td>U_2NiSi_3</td>
<td>153</td>
<td>360</td>
<td>1260</td>
<td>1319</td>
</tr>
<tr>
<td>UFeSi</td>
<td>394</td>
<td>706</td>
<td>1239</td>
<td>1479</td>
</tr>
<tr>
<td>UNiSi</td>
<td>309</td>
<td>405</td>
<td>1248</td>
<td>1348</td>
</tr>
<tr>
<td>U_2Fe_3Si</td>
<td>719</td>
<td>955</td>
<td>762</td>
<td>1417</td>
</tr>
<tr>
<td>UNi_2Si_6</td>
<td>591</td>
<td>557</td>
<td>850</td>
<td>1175</td>
</tr>
<tr>
<td>UFe_2</td>
<td>683</td>
<td>1054</td>
<td>—</td>
<td>1256</td>
</tr>
<tr>
<td>UNi_2</td>
<td>698</td>
<td>880</td>
<td>—</td>
<td>1123</td>
</tr>
</tbody>
</table>

The calculations were performed also on the compounds where \(T\) element is Fe in order to confront the results in an isostructural series of compounds. The distances were determined using the atomic positions reported in [1, 2,14].

5. DISCUSSION

The discussion on \(V_{\text{ff}}\) values is proper inside the isostructural series of compounds. For \(U_2TSi_3\) compounds \(V_{\text{ff}}\) has low values and very close inside the group. The \(V_{fp}\) presents high values but very close even the magnetic properties are different. The \(V_{fd}\) varies and has lower value for increasing 3d electron number indicating the diminishing of the fd orbitals overlap. For \(U_2FeSi_3\) the covalent energy \(V_{\text{total}}\) (1.36 eV) is close to the critical energy for \(5f^3\) configuration (1.38 eV); the compound has no magnetic moment on the uranium positions and presents the characteristics of the spin fluctuations.
Magnetic behaviour of U(Ni$_{x}$Si$_{1-x}$)$_2$ system

The compound where T=Ni is magnetically ordered and this fact is supported by the covalent calculated energy inferior to the critical limit. In the UTSi class $V_{fd}$ is decreasing as the d electrons number becomes higher. This statement is analogous to the Hill criterion which assumes that for UU interatomic distances larger than 3.5 Å there is no direct overlap of 5f wave functions. The intense change occurs in $V_{fd}$ values, a large magnitude is found for nonmagnetic compound UFeSi and a decreased value for the ordered system with Ni. $V_{total}$ according to the magnetic state criterion indicates a nonmagnetic compound for UFeSi and a magnetic one for UNiSi. In the systems having x=0.75 the different magnetic properties are supported by large decreasing in the $V_{fd}$ values rising Z. The covalent energy is lower than the critical limit for the system containing Ni supporting the U magnetic moment existence. For U$_2$Fe$_3$Si $V_{total}$ indicates no ordering and the system shows spin fluctuations behaviour. The criterion of comparing the $V_{total}$ to the critical energy for 5f$^2$ configuration seems to be proper for the presented systems. For the parent systems the criterion is also respected indicating no U magnetic moments in USi$_2$ with $V_{total}$ superior to the critical energy and ordering presence in UNi$_2$ and UFe$_3$ with lower $V_{total}$ values.

![Graph showing composition dependence of transition temperature and $V_{fd}$ values](image)

**Fig. 3 -** The composition dependence of the transition temperature and $V_{fd}$ values for U(Ni$_{x}$Si$_{1-x}$)$_2$ system

Regarding the system U(Ni$_{x}$Si$_{1-x}$)$_2$ we follow the composition dependence of $V_{fd}$ as a measure of f-d hybridization as well as the composition dependence of the transition temperature as it is illustrated in Fig.3.

There is possible to remark a correspondence in their opposite changing especially for $x \geq 0.5$ which evidences the importance of f-d hybridization in describing the magnetic order state in these compounds.

**Acknowledgement:** This work is partially supported by IFA under CERES 10/C1-2001 project.
REFERENCES

1. B.CHEVALIER, R.PÜTTGEN, B.DARRIET, P.GRAVEREAU, J.ETOUNEAU, Structural chemistry and magnetic behaviour of the ternary silicides U$_2$TSi$_3$ (T = Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Au), J. Alloys Compound. 233, 150, 1996
2. F.CANEPÀ, P.MANFRINETTI, M.PANI, A.PALENZONA, Structural and transport properties of some UTX compounds where T=Fe,Co,Ni and X=Si,Ge, J. Alloys Compound. 234, 225, 1996
5. V.H.TROČ, R.TRAN, Magnetic properties of UT(Si,Ge) series, J. Magn. Magn. Mater. 73, 389, 1988
8. J.J.M. FRANSE, R.GERSDORF, Landolt Börnstein III/19F1, Actinide Elements and their Compounds with other Elements, p. 117-119