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HIGH ENERGY SPECTROSCOPY INVESTIGATION OF SOME TERNARY Ce SYSTEMS

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Résumé - Nous présentons des mesures de seuil LIII et de photoémission 3d dans les alliages (Ce, La)Ru2Si2 et (Ce, Y)Ru2Si2. Nous montrons que les variations de valence et d’hybrïdation f-d sont peu importantes dans ce système qui reste presque trivalent. Dans ce contexte, la forte variation des propriétés macroscopiques de ces alliages (telle que susceptibilité magnétique) se produit lorsque l’écart entre les niveaux de champ cristallin et la température Kondo sont du même ordre de grandeur.

Abstract - LIII absorption and 3d photoemission results are presented for the alloys (Ce, La)Ru2Si2 and (Ce, Y)Ru2Si2. We show that valence and f-d hybridization variations are modest in this system where Ce remains nearly trivalent. In this context, strong variations in the macroscopic properties of these alloys (eg magnetic susceptibilities) are attributable to a cross-over between crystal field levels splitting and Kondo temperature.

I - INTRODUCTION

Cerium intermetallic compounds CeM2Si2 with the ThCr2Si2-type tetragonal structure have recently focussed many studies since all the various fascinating properties of cerium systems can be found in the series: superconducting heavy fermion system (M = Cu), mixed valence (M = Co, Ni...), magnetic ordering (M = Au, Pd...). Within these compounds, CeRu2Si2 is peculiar since macroscopic measurements (lattice constant, susceptibility, thermopower...) have shown that it lies on the border-line between a trivalent and a mixed valent ground state, and presents at low temperature the so-called Kondo lattice behaviour /1, 2/. As a consequence a weak perturbation (pressure, alloying, magnetic field...) produces a transition either to mixed-valent or to trivalent state.

We present here 3d core level photoemission and LIII absorption on Ce1-xYxRu2Si2 (where Ce is non-magnetic) and Ce1-yLa2-yRu2Si2 (where Ce is magnetic for y ≥ 0.2) and compare the results with those obtained from macroscopic measurements/ 2 / (magnetic susceptibility, specific heat...).

II - EXPERIMENTAL

Ce1-yLa2-yRu2Si2 and Ce1-xYxRu2Si2 samples with y = 0, 0.1, 0.2, 0.3, 0.5, 0.7, 0.9 and x ≥ 0.1, 0.2, 0.4, 0.5, 0.7 and 0.9 have been prepared by arc melting. LIII absorption experiments have been carried out at LURE on the EXAFS II station using the Si (311) double crystal monochromator. UHV (P = 10^-10 torr) photoemission
have been performed in a VG ESCA III apparatus using Al K$_\alpha$ radiation with an energy resolution of 1 eV. Samples were cleaned by cycling argon ion bombardment and heating to 400°C in order to limit oxygen contamination ($\leq 5\%$) and preferential sputtering. For the XPS study, we used polycrystalline CeRu$_2$Si$_2$ and Ce$_{0.6}$Y$_{0.4}$Ru$_2$Si$_2$ samples and a monocrystalline Ce$_{0.7}$La$_{0.3}$Ru$_2$Si$_2$ (001) surface.

III. RESULTS

a) $L_{III}$ absorption

The $L_{III}$ spectra of (Ce,T)Ru$_2$Si$_2$ alloys exhibit a main resonance near 5720eV due to $2p^64f^1 \rightarrow 2p^54f^1 5\text{cd}^2$ transitions and a shoulder at 10 eV higher energy characteristic of $2p^64f^0 \rightarrow 2p^54f^0 5\text{cd}^2$ transitions. The relative weight of $4f^1$ and $4f^0$ contributions $C_1$ and $C_0$ have been estimated by a fit of the "white line" /3/. For metallic Ce systems, the values obtained by this method agree qualitatively with those used to fit other spectroscopic experiments (3d XPS, UPS, BIS, Mu absorption) /7/ so that, as a first approximation, we shall identify $C_1$ with the fractional occupation of $4f$ states in the ground state ($n_f$).

These values of $n_f$ are reported on Fig. 1 as a function of the reduced volume $\log V/V_0$ ($V_0$ refers to CeRu$_2$Si$_2$). It is remarkable that in the whole concentration range, the $4f$ occupancy varies smoothly from $n_f = 0.825$ (Ce$_{0.1}$Y$_{0.9}$Ru$_2$Si$_2$) to $n_f = 0.95$ (Ce$_{0.1}$La$_{0.9}$Ru$_2$Si$_2$) with a slight knee corresponding to the critical concentration for the onset of magnetism ($y = 0.15$). It can be concluded that the chemical pressure in this system is not strong enough for a valence saturation as observed eg in Ce(Pd,Rh)$_3$ alloys /6/. This valence saturation regime is observed in the series for the compounds CeNi$_2$Si$_2$, CeCo$_2$Si$_2$ and CeFe$_2$Si$_2$ (see inset of fig 1 and /5/). As a consequence, $n_f$ is not far from unity in CeRu$_2$Si$_2$ alloys and justifies a posteriori a Kondo type description of the macroscopic properties /2/. These results also confirm that an integer valence is not a necessary condition for a magnetically ordered ground state at low temperature since samples with $y \geq 0.2$ antiferromagnetically order below $T_N \leq 5$ K; this effect is also known for some Eu or Yb compounds (for a theoretical discussion see /7/).

![Graph](image)

Fig. 1: Zero temperature extrapolated magnetic susceptibility (full symbols) and $4f$ count deduced from $L_{III}$ (open symbols) in Ce$_{1-x}$Y$_x$Ru$_2$Si$_2$ (squares) and Ce$_{1-y}$La$_y$Ru$_2$Si$_2$ (circles) as a function of the reduced volume ($V_0$ for CeRu$_2$Si$_2$). The lines are a guide to the eyes. Typical spectra and variations of $n_f$ as a function of the unit cell volume for CeNi$_2$Si$_2$ and Ce$_{1-x}$La$_y$Ru$_2$Si$_2$ in inset.
b) 3d photoemission

![3d photoemission spectra for Ce\textsubscript{0.4}Ru\textsubscript{0.6}Si\textsubscript{2}, CeRu\textsubscript{2}Si\textsubscript{2}, and Ce\textsubscript{0.3}La\textsubscript{0.7}Ru\textsubscript{2}Si\textsubscript{2}. The 4f\textsubscript{2} satellite is indicated by an arrow; lines are a guide to eyes.]

A small peak is also found 11 eV above the main 3d photoemission line in CeRu\textsubscript{2}Si\textsubscript{2}, Ce\textsubscript{0.7}La\textsubscript{0.3}Ru\textsubscript{2}Si\textsubscript{2} and Ce\textsubscript{0.6}Ru\textsubscript{0.4}Si\textsubscript{2}, and can be attributed to the 4f\textsuperscript{2} configuration. Its relative intensity C\textsubscript{0} < 10% agrees qualitatively with L\textsubscript{III} edge results. Because of the overlap of this peak with the 3d\textsubscript{5/2} line, we only represent on the Fig. 2 XPS spectra around the main 3d\textsubscript{5/2} peak. A satellite is clearly seen 6 eV below the main line with roughly the same weight in the three alloys. The occurrence of this satellite is a common feature of Ce (and other light Rare Earth) compounds and is due to the possible screening of the 3d core-hole by 4f orbitals \cite{8}. An interpretation of this phenomenon, based on the one impurity Anderson model has been proposed and applied to various intermetallics \cite{7}. A comparison with computed spectra for systems similar to CeRu\textsubscript{2}Si\textsubscript{2} is consistent with an hybridization parameter \( \Delta \approx 80 \) meV for the three alloys of Fig. 2.

IV - DISCUSSION

Macroscopic measurements on the system (magnetic susceptibility and specific heat) \cite{2} allow to distinguish two cases: (i) samples \( y \geq 0.2 \) where antiferromagnetic ordering competes with Kondo coupling \( T_\text{K} < 3 T_\text{N} \); these alloys will not be considered in the following; (ii) in the other cases, a nearly constant magnetic susceptibility \( \chi_0 \) is found at low temperature, and, as one goes towards \( Y, \text{CeRu}_2\text{Si}_2 \), the occurrence of a free ion magnetic behaviour is gradually suppressed as \( \chi_0 \) decreases by one order of magnitude (see Fig. 1), what has been interpreted by a rising of \( T_\text{K} \) (10 K - 300 K).

Let us now relate the previous spectroscopic results with these macroscopic measurements. Using an 1/\( N_\text{f} \) expansion of the one impurity Anderson model \( (N_\text{f} \) is the degeneracy of 4f states), the values of \( n_\text{f} \) can be approximately related to \( \Delta \) and to \( \chi_0 \); the zero temperature extrapolated susceptibility (also represented in Fig. 1 and of course defined only when the ground state is non-magnetic) \cite{7}:

\[
N_\text{f} \Delta = \frac{\pi C}{\chi_0} \frac{n_\text{f}^2}{1-n_\text{f}}
\]

(1)

C is the Curie constant relevant to \( N_\text{f} \); \( n_\text{f} \) should be obtained at 0 K for consistency, however, we observed on CeRu\textsubscript{2}Si\textsubscript{2} only a slight decrease of \( n_\text{f} (2 \%) \) in the temperature range 300 K - 4.2 K, so that, for simplicity, we neglected these valence variations. A simple numerical application with our experimental data suggests that \( \Delta \) varies from 60 meV for Ce\textsubscript{0.10}La\textsubscript{0.9}Ru\textsubscript{2}Si\textsubscript{2} to 17 meV for CeRu\textsubscript{2}Si\textsubscript{2}. This concentration variation of \( \Delta \) is much larger than those estimated for the \( \alpha_\text{Au} \) transition of metal Ce \cite{9} and is apparently conflicting with those deduced from photoemission data. However, it is important to note that at this stage that the formula (1) does not take into account the eventual splitting of 4f\textsuperscript{1} levels by the crystal-
lyne field. In a tetragonal solid, the ground state of trivalent Ce is splitted into three doublets as a result of crystal field interaction. But the effective degeneracy \( N_f \) that enters in (1) is not obvious to define when the hybridization parameter reaches the same order of magnitude as the crystal field levels splittings \( \Delta_1 \) and \( \Delta_2 \).

From an experimental point of view, we must consider separately the following situations:

- **Kondo systems** : (CeRu\(_2\)Si\(_2\), CeCu\(_6\),...) the formation of a Kondo singlet at low temperature can be identified (eg by specific heat measurements), and at higher temperature, crystal field excitations occur /2/. In such a case the "effective" degeneracy is \( N_f = 2 \) for \( T << \Delta_1,\Delta_2 \) and \( N_f = 6 \) for \( T >> \Delta_1,\Delta_2 \).

- **Mixed-valent systems** : (CeSn\(_3\), CeNi, CeTi\(_2\),...) crystal field excitations are not clearly observed /12, 13/. The use of \( N_f = 6 \) and \( 1/N_f \) expansions even at low temperature seems to be a valuable approximation for these systems.

In the present situation, the characteristic temperature \( T_K \) can be related to the three-level splitting by the following approximate relation /11/:

\[
\left( \frac{T_K}{D_0} \right)^2 \left[ \frac{\langle \tau_K + \Delta_1 \rangle}{\langle D_0 + \Delta_2 \rangle} \right]^2 = \text{exp}(-1/\rho J)
\]

\( D_0 \) is an energy cut off and \( \rho J \) can be expressed as a function of the Anderson Hamiltonian parameters:

\[
\rho J = \left( \frac{2 \Delta/\pi e_f^2}{\rho} \right) + \left( \frac{2 \Delta/\pi (U_{ff} - e_f^2)}{\rho} \right)
\]

with a set of parameters relevant for Ce alloys \( (e_f = 2 \text{ eV}, U_{ff} = 5 \text{ eV}, D_0 = 10^4 \text{K}, \Delta_1 = 220 \text{ K} \text{ and } \Delta_2 = 600 \text{ K}) /2/ \), one gets : \( \Delta = 75 \text{ meV} \) for \( T_K = 24 \text{ K} \) (i.e. CeRu\(_2\)Si\(_2\)) and \( \Delta = 105 \text{ meV} \) for \( T_K = 300 \text{ K} \) (i.e. \( \Sigma \text{CeRu}_2\text{Si}_2 \)).

V - CONCLUSION

As a conclusion we suggest that the transition observed in the magnetic behaviour of CeRu\(_2\)Si\(_2\) alloys can be interpreted by a cross-over between the crystal field level splitting and the Kondo temperature, due to a slight increase of the hybridization parameter as the unit cell volume decreases. This cross-over produces a rising of the effective degeneracy of 4f states from 2 to 6. However, at room temperature \( (kT > \Delta) \), the effective degeneracy that enters for the interpretation of 3d photoemission can be thought to be close to 6, and the conclusions deduced from comparison with \( 1/N_f \) expansion calculation (weak variations of \( \Delta \sim 80 \text{ meV} \)) are valid and agree with the above discussion.

REFERENCES

/3/ J. Röhrler, ibid ref. /1/, p. 175.