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EVIDENCE OF VALENCE FLUCTUATIONS IN YTTERBIUM BASED AMORPHOUS ALLOYS

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Abstract. – In this paper, we present magnetic and L_{III} edge measurements on two amorphous ytterbium based systems: Yb-Pd and Yb-Si. In the crystalline compounds of both systems, ytterbium ions exhibit valence fluctuations and we show that this anomalous electronic configuration is basically preserved in the corresponding amorphous alloys.

The hybridization between 4f localized and extended states induces an intermediate valent ground state (IV) in many rare-earth (RE) based compounds. Local environment parameters are known to play an important role on these phenomena. Nevertheless, the sensitivity of such a ground state to topological disorder is not definitely established. Several studies have shown that europium valency is very sensitive to disorder: the two integer valent states are generally stabilized in amorphous alloys [1, 2] and then, the Eu intermediate valence seems to be incompatible with the amorphous structure. The aim of this study is to analyse the influence of structural disorder on ytterbium valence fluctuations. We investigate the Yb electronic configuration in amorphous phase by two complementary techniques: the average valency can be obtained independently from L_{III} edges and magnetic measurements. The comparison of data from both experiments allows to determine the nature of the valence admixture (valence fluctuations or inhomogeneous admixture of integer valent states).

Amorphous alloys of nominal composition Yb_xPd_{1-x} ($0.29 \leq x \leq 0.60$) and Yb_xSi_{1-x} ($0.10 \leq x \leq 0.70$) were obtained by vapour-quenching onto liquid nitrogen cooled substrates under high vacuum (10^{-8} Torr) conditions. The X-ray absorption measurements on the ytterbium L_{III} edge were carried out in LURE; the spectra were recorded at room temperature with an energy resolution of about 1.5 eV. Magnetic measurements were performed with a SQUID magnetometer in the temperature range 1.6-300 K.

It was recently proposed that the crystalline YbPd compound exhibits a rather singular behaviour of intermediate valence ($V = 2.8$) coexisting with low-temperature magnetic ordering [3]. From Mössbauer experiments, Bonville *et al.* showed that actually two charge states coexist in equal proportion [4]: one being magnetic and the other non-magnetic. As trivalent state is expected for the magnetic ions, the non-magnetic ones must have an average valence of 2.6 in order to reproduce the value obtained from L_{III} edge (2.8) for this compound. We found that a similar valence admixture occurs in the disordered Yb_xPd_{1-x} alloys. In figure 1, inverse susceptibilities are shown for several alloys. A curie-Weiss law (CW) with a very weak paramagnetic Curie temperature ($\theta \cong 0$ K), is clearly observed. This behaviour reflects the presence of paramagnetic trivalent ions whose amount, deduced from the CW constant, is shown in figure 2. The composition dependence of the L_{III} average valence is also reported in this figure. The disagreement between both sets of values indicates that the measurements cannot be explained by a simple admixture of triva-

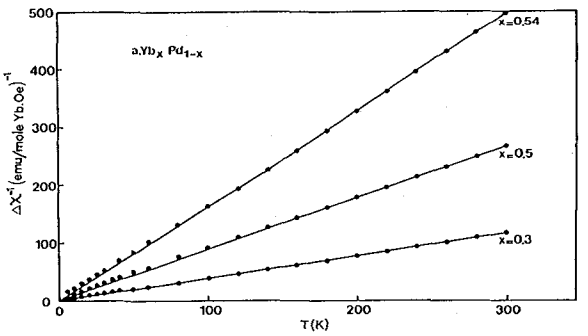


Fig. 1. – Inverse susceptibilities for several amorphous Yb-Pd alloys.

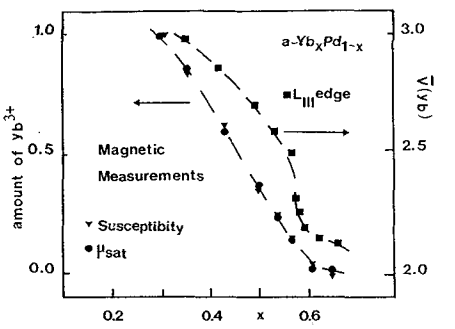


Fig. 2. – Comparison between the amount of trivalent ions and the average valence.

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lent and divalent ions. Therefore, a subtle valence admixture, reminiscent to that encountered in the YbPd compound, occurs in the amorphous alloys. Then the fractions of different charge states for each composition can be deduced (Fig. 3). The amount of trivalent ions is obtained from magnetic measurements whereas the divalent and intermediate valent (IV) fractions are estimated from the comparison with L_{III} edge results with the assumption that IV ions have a composition independent valency of 2.6 like in the crystalline YbPd compound. The fraction of IV ions is found to be maximum at about $x = 0.50$. This result shows that, in contrast to Eu case, the ytterbium valence fluctuations can survive in the presence of structural disorder. This conclusion is confirmed by the study of the Yb-Si system.

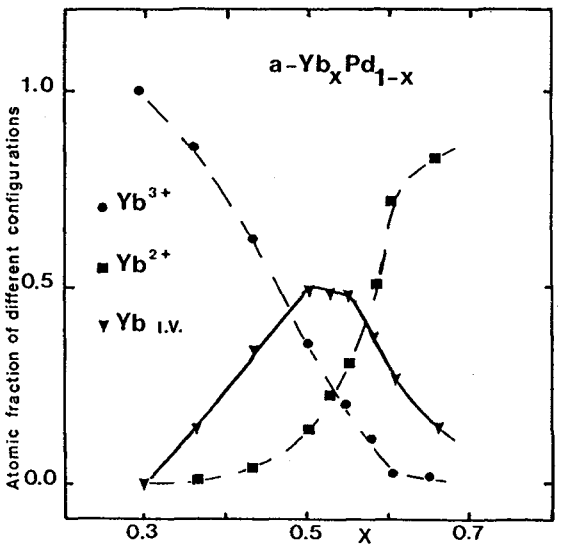


Fig. 3. – Fractions of the different charge states *versus* composition in the amorphous Yb-Pd alloys.

In the crystalline YbSi, Yb_3Si_5, Yb_5Si_3, Yb ions exhibit charge fluctuations. In the figure 4, we have reported the ytterbium valence obtained from *X*-ray absorption spectroscopy. Ytterbium ions in concentrated alloys are nearly divalent like Yb metal. The average valency increases with decreasing Yb content, exhibits a maximum around $x = 0.50$ and tends towards the divalent state for the dilute alloys. The valence admixture in these Yb_xSi_{1-x} amorphous alloys is less complicated than that in the amorphous Yb_xPd_{1-x} alloys. Indeed, magnetic measurements show only a small amount of trivalent ions which vanishes below $x = 0.3$. XANES studies confirm this homogeneous valence admixture [5]. These results show that a pure intermediate valent state can exist in a strongly disordered system.

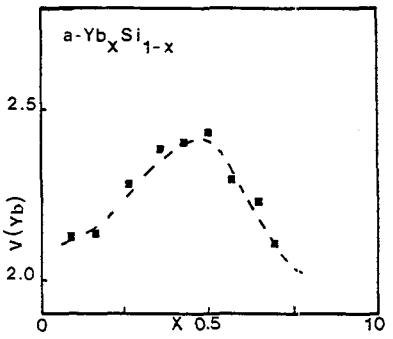


Fig. 4. – Mean valence in the amorphous Yb-Si alloys.

Let us mention that the hybridization of the 4f states with the conduction electrons is the dominant parameter in valence instabilities phenomena. It is generally admitted that this electronic coupling progressively decreases across the lanthanide series according to the 4f wave-function contraction. Nevertheless in Yb systems, hybridization induces an increase in the number of 4f electrons. Then, in strongly intermediate valent systems, the tail of the 4f wave-functions is more important than for the trivalent Yb ions [6]. As a consequence, the overlap with the neighbour orbitals is enhanced leading to an increase of the hybridization strength which becomes comparable to that encountered in cerium systems (a value of 90 meV was proposed for the $YbAl_3$ compound [6]). Moreover, as the energy difference between the $4f^{13}$ and $4f^{14}$ configuration is smaller than that in the cerium systems, the electronic configuration must be very stable and is not affected by structural disorder.

Acknowledgments

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