# SIZE VERSUS DISORDER EFFECTS IN THE ELECTRONIC PROPERTIES OF NANOSIZED INTERMEDIATE VALENCE METALS

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Nanotechnology is deeply attached to the knowledge of basic mechanisms driving the change of materials properties. For the case of magnets, the properties are drastically modified by the size of the particles and several behaviours can be found, which are object of huge attraction [1]. On the one hand, the coupling between the shell and the core of the particles may affect the superparamagnetic limit [2]. If we study the interparticle magnetic coupling, this is frequently governed by dipolar and/or RKKY interactions, which strongly affects a very important technological magnitude as anisotropy [3]. In other cases, it is the intrinsic magnetic clustered nature of the metal the origin of many magnetic properties in the border of non Fermi liquids, displaying step-like hysteresis loops in the miliKelvin range [4]. But those interesting effects are not restricted to artificial structures; for example they are also found in goethite, a very common mineral in the surface of earth, of great importance for archaeology, biosciences or geology, to cite a few areas [5]. Over the last years we have gathered some experience in dealing with these complex magnetic systems and the arising and persistent key question is whether the size or the disorder in the crystallographic structure is the main driving parameter acting in the magnetic properties. This dilemma is clearly a challenge for a broad number of scientists.

Recently we have undergone an ambitious program to study in detail the properties of Strongly Correlated Electron Systems over a certain range of particle sizes. These materials are characterized (in bulk) by a large effective electron mass, displaying in some cases exotic behaviours, such as non-Fermi liquid or Quantum Critical Points [6]. They also exhibit an interesting competition of the exchange (RKKY) and Kondo interactions, leading to magnetic-nonmagnetic crossovers that can be tuned by different physical (and chemical) parameters. Most of these systems are based in an attractive situation, specific of Ce ($4f^1$, one electron) and Yb ($4f^{13}$, one hole) atoms, which in some cases present intermediate valence [4].

In our study, we have prepared a series of alloys of $YbAl_3$ (cubic) in different sizes from bulk to 10 nm, as estimated from Rietveld refinements of XRD data, without noticeable change in the lattice parameter ($a$ = 4.2057(7) Å). The magnetic susceptibility (2-300K) presents the typical intermediate valence behavior with a peak shifting in temperature with particle size. Also the specific heat (2-300 K) shows modifications in the usually labelled as Kondo temperature and the electronic contribution. To dig in the microscopic origin, X-ray absorption (XANES and EXAFS) were carried out in the beamline BL39XU (Spring8, Japan) and BM25A (ESRF, France) on the Yb-$L_{II}$ and Yb-$L_{III}$ edge. The short-range EXAFS Foruier transforms shows the existence of constant Yb-Yb distance (2.96 Å) whereas the Debye-Waller factor increased from 0.0069(22) $Å^2$ (bulk alloy) to 0.0115(21) $Å^2$ in samples with 10 nm. Concomitantly, the valence decreased in the XANES spectra with decreasing size. The analysis of the variations of the main parameters (valence, electronic contribution ot the specific heat, Kondo temperature) is in full agreement with the size factor as a driving force and atoms in the surface (Yb2+) play an enhanced role when the ratio surface atoms/volume atoms is increased. In consequence for this case alloy in the verge of magnetism, it is the size the main parameter.

**References:**

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**Figures:**

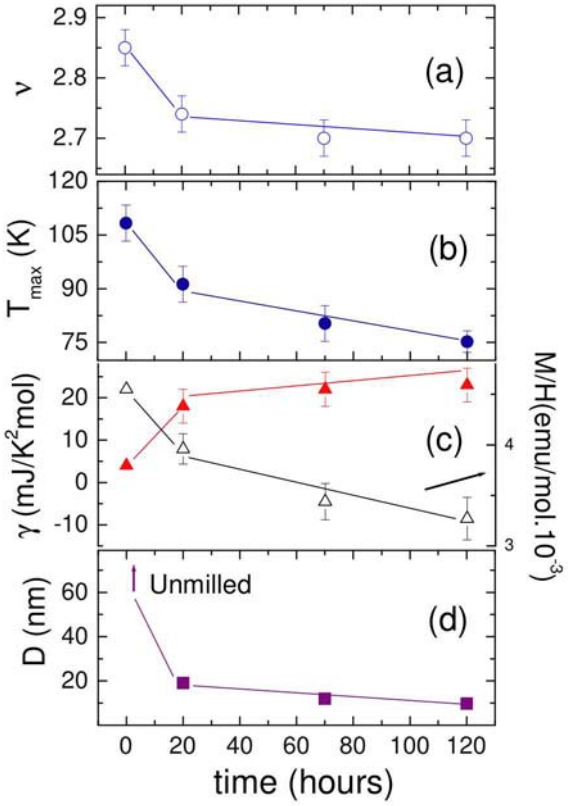


**Figure.** Milling time dependence of the mean valence v, T*max* of the magnetic contribution to the specific heat (b), the Sommerfeld coefficient ($\gamma$) of the electronic contribution and the absolute value of the magnetic susceptibility at the maximum (c), and the size of the particles (D) (d). The grain size of the unmilled alloy can only be suggested (arrow). An abrupt variation from unmilled to 20 hours, followed by a smooth change on going to 120 hours milled alloy is observed. Lines are guides for the eye.