Magnetization and specific heat of nanocrystalline rare-earth TbAl$_2$, TbCu$_2$ and GdAl$_2$ alloys

D. P. Rojas, L. Fernández Barquín, J. Rodríguez Fernández, J. I. Espeso and J. C. Gómez Sal
DCITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain.
E-mail: rojasd@unican.es

Abstract. Measurements of the magnetization and specific heat on nanocrystalline TbAl$_2$, TbCu$_2$ and GdAl$_2$ with mean particle diameters below 40 nm show a different behavior from those made on bulk alloys. A reduction of the saturation magnetization quantified in TbAl$_2$ from 8.4 $\mu_B$/mol for the bulk to 5.8 $\mu_B$/mol for a 14 nm alloy is attributed to a spin disordered layer on the particle surface. In the specific heat, the lambda anomaly associated to the ferro (\(\Delta c = 6.6\) J/molK, 9.8 J/molK) and to the antiferromagnetic transitions (7.1 J/molK) in the bulk samples, respectively, is smeared out due to finite size effects.

1. Introduction
The magnetic nanocrystalline materials are being object of an intense research [1]. However, this activity is overwhelmingly focused on systems including 3d elements, leaving behind the attractive modifications of magnetic properties in nanometric rare-earth alloys [3, 4, 5, 6, 7]. In these materials, due to a larger fraction of the atoms at the interface when the size of the samples is reduced, the physical properties closely related to the atomic structure reveal differences when compared to bulk materials [1, 2].

First steps in the study of nanosized rare-earth alloys were carried out on the GdAl$_2$ system, where the long-range ferromagnetism disappears giving rise to a spin-glass behavior at lower temperatures concomitant with the grain size reduction [3]. Further studies attributed this glassy behavior to the intrinsic properties of chemically disordered GdAl$_2$, or to the extrinsic ones, determined by the nanostructure [4]. Additionally, the role of the disorder-induced random exchange and anisotropy was also considered [5]. A similar situation was also observed in the ferromagnetic polycrystalline TbAl$_2$ material, where the long-range ferromagnetic structure at $T_C = 105$ K is inhibited in favor of a disordered spin arrangement below 45 K with the reduction of the particle size [6]. Another example is the antiferromagnetic TbCu$_2$ ($T_N = 49$ K) where the ball-milled alloy showed a glassy behavior below 15 K [7].

In the present work, we will give further insight by selecting three different rare-earth alloys, namely TbAl$_2$, TbCu$_2$ and GdAl$_2$, of cubic and orthorhombic crystallographic structures and with ferro and antiferromagnetic behaviour in the bulk state. This will enable a comparison using the results of the magnetization and, more interestingly, of the specific heat measurements. These results may be relevant for further studies using microscopic techniques such as Mössbauer spectroscopy [8] or small angle neutron scattering (SANS) [9], as performed in nanocrystalline Gd.
2. Experimental details
The starting alloys were first prepared in an arc furnace from stoichiometric amounts of Tb (3N Alfa), Gd (3N, Alfa), Cu(5N, Alfa) and Al (5N, Alfa) metals. The resulting alloys were crushed and milled in a planetary high-energy ball system as already described in [6]. The maximum milling time depends on the mechanical properties of the alloy, with a maximum of 300 hours for TbAl$_2$. X-ray diffraction measurements with MoK$_\alpha$ radiation were carried out on a Brucker D8 Advance diffractometer equipped with a vacuum sample holder. The field-dependence of the magnetization was measured at 5 K (up to 9 T), and the specific heat ($c_p$) measurements were done between 20 K and 220 K, in order to focus on the eventual variations in the ferromagnetic transitions of TbAl$_2$(105 K)[6], GdAl$_2$ (164 K) and antiferromagnetic transition of TbCu$_2$ (49 K)[7].

![X-ray diffraction patterns for bulk and 70 hours GdAl$_2$ milled alloys. In the inset, the milling time dependence of the grain size for TbAl$_2$, TbCu$_2$ and GdAl$_2$ milled alloys, is depicted. The line is a guide for the eyes](image1)

Figure 1. X-ray diffraction patterns for bulk and 70 hours GdAl$_2$ milled alloys. In the inset, the milling time dependence of the grain size for TbAl$_2$, TbCu$_2$ and GdAl$_2$ milled alloys, is depicted. The line is a guide for the eyes.

3. Results and Discussion
The milling process results in nanometric particles as reported previously [6] and shown here for GdAl$_2$ in Figure 1. In the latter case, the particles are similar to those obtained with a vibrating frame [3]. In the inset of Figure 1, the milling time required for every sample to reach a nanometric size is compared. It is evident that nanocrystalline TbCu$_2$ is easily obtained, probably due to the ductile nature of this alloy.

As commented in the introduction, drastic changes in the magnetic properties are observed with the reduction of the particle size, as shown in Figure 2. A relationship between the size and the magnetization was already suggested by the results on TbAl$_2$ alloys obtained from four different milling times [6]. Bearing in mind those results, we can establish here a quantitative correlation using the estimated fraction of the atoms at the surface of the particles with respect to those in the total volume with the magnetization reduction. It is striking to note that the reduction in the saturation magnetization ($M_S$) scales with the inverse of the diameter (D) of the particles, as shown in Figure 3. Consequently, considering that the fraction of the surface atoms is also inversely proportional to the size D [1, 2], a direct relationship between this reduction and
the fraction of surface atoms can be established in three different rare-earth alloys. This could be a sign of a surface spin demagnetization due to disorder, in a similar way to that observed in nanometric ferrimagnetic oxides of transition metals [10, 11]. The random anisotropy disorders the spins at the surface of each particle but the structural arrangement is a collection of particles separated by a grain boundary in which the disorder is strong due the combination of surface disorder of every particle[2].

![Figure 2](image-url)

**Figure 2.** Field dependence of the isothermal magnetization curves at 5 K for TbAl$_2$, GdAl$_2$ and TbCu$_2$ milled alloys.

The specific heat is particularly sensitive to magnetic transitions. The jump $\Delta c$ at the magnetic transitions for bulk alloys shows a noticeable reduction with the decrease of the particle size, as shown in Figure 4. For TbAl$_2$ alloys, the decrease of $\Delta c$ ranges from 6.6 J/molK in the bulk to 0.4 J/molK in the 39 nm sample. The lambda anomaly practically disappears for mean grain sizes of 27 nm, 15 nm and 25 nm, for TbAl$_2$, TbCu$_2$ and GdAl$_2$, respectively. This behavior resembles the one obtained in the calorimetric study of CoO magnetic nanoparticles [12]. These results can be explained by the presence of finite-size and surface effects, which become more relevant with the decrease of the size of the particles, and therefore also affect the thermal properties, as shown by Monte Carlo simulations for ferrimagnetic nanoparticles [11]. In addition, structural disorder at the atomic scale inside the particles, which has been discussed in GdAl$_2$[3], may also affect the magnetic state. More evidences in this sense were gathered in TbAl$_2$, showing the presence of an intrinsic disordered magnetic state inside the particles [6]. For both cases, the experimental evidences only came from magnetization measurements. Indeed, a combination of magnetization and $c_p$ in YbAl$_3$ (non magnetic) nanoparticles revealed that the surface contribution is of paramount importance [13]. The smearing of the transition observed here is in fact commented in the results for 3d-alloys, where the nanocrystalline magnetic nanoparticles are embedded in an amorphous matrix acting as grain boundaries [14]. Research to understand in more detail this attractive variation of the $c_p$ is already in progress.

4. Conclusions
The results presented above show the influence of the surface effects on the magnetic and thermal properties of nanosized rare-earth TbAl$_2$, TbCu$_2$ and GdAl$_2$ alloys. These effects are manifested through a distinct behaviour, different from those of bulk materials. The decrease of the $M_S$ can be associated to the existence of a grain boundary among the nanoparticles and the decrease of
**Figure 4.** Temperature dependence of the specific heat curves for TbAl$_2$, TbCu$_2$ and GdAl$_2$ bulk and nanometric size alloys around the magnetic transitions.

the lambda anomaly of the $c_p$ to finite-size effects together with a evolution into a spin disordered arrangement with the decrease of the particle size.

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