Phonon softening on the specific heat of nanocrystalline metals

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In nanocrystalline (nc) metals with particle sizes below 5 nm and $T \leq \Delta$ ($\Delta$ is the average electronic level spacing), the quantum electronic effects seem to strongly influence the thermodynamic properties at low temperatures [1]. However, at higher temperatures for $T \gg \Delta$ and/or sizes above 5 nm, the level distribution becomes irrelevant and the influence of size effects on the specific heat can be basically attributed to phonons. It is expected that at the surface of particles the loss of bonding of atoms leads to a modification of the phonon modes, affecting the thermodynamic properties, such as the specific heat. In this sense, specific heat measurements in the temperature range between 150 and 300 K on nc-Pd (6 nm) and Cu (8 nm) have revealed higher values than in the polycrystalline state, which was attributed to the contribution of the interface [2].

It is worth commenting that the experimental results reported in nc-metals have been constrained to this enhancement above 150 K, and no experimental evidences about a low temperature anomaly, which has only been described theoretically [3], were reported before our results [4,5]. Our first step towards the understanding of this issue was addressed very recently in the study of the influence of size effects on the physical properties of the YbAl$_3$ intermediate valence material [4]. In particular, a low temperature peak around 40 K in the specific heat was derived from the analysis of changes on the magnetic contribution of nanosized samples. However, this last result may be affected by the complicated electronic structure of these alloys.

For this reason, we have extended our studies to more simple systems as common metals Cu, Fe and Ni in order to give a full description of the behaviour of the specific heat in all temperature ranges [5].

The results of measurements in bulk and nc-Fe, Cu, Ni and LaAl$_3$ alloy have shown an excess specific heat in the nanosized samples. In addition to a slope increase at high temperatures ($T > 150$ K), already reported in some nc-metals, a peak at low temperatures between 20 and 65 K is clearly observed. The analysis of the specific heat curves indicates that the experimental data are in good agreement with a model which considers contributions from the grain boundary and core atoms in the nanoparticles. This model is supported by Raman spectroscopy measurements, indicating the presence of a softening of phonon modes at the surface in the nc-samples associated with a size reduction and increase of the atomic disorder.
References

Figure 1

TEM image of nc-LaAl₂ showing nanoparticles with a mean size of 12 nm. In the insets, details of the distribution of the particle sizes (above right) and high resolution TEM images of a particle (below right) are given. The interatomic distance between lattice planes inside a particle is around 0.5 nm.

Figure 2

Temperature dependence of the difference of the specific heat between the bulk and nc-Cu (32 nm). A peak at 50 K and a contribution (slope increase) above 150 K are observed. In the inset, the plot of c/T versus T² evidencing the change in the slope, and therefore in ℏ₀, is presented. Lines are just guides for the eyes.

Figure 3

Raman spectrum of nc-Fe (20 nm) at 300 K showing overtones of acoustic phonons (TA₁ and TA₂) in the f–N direction and LA in the f–P ones. The solid lines are the result of the fitting of the peaks with Lorentzian functions.