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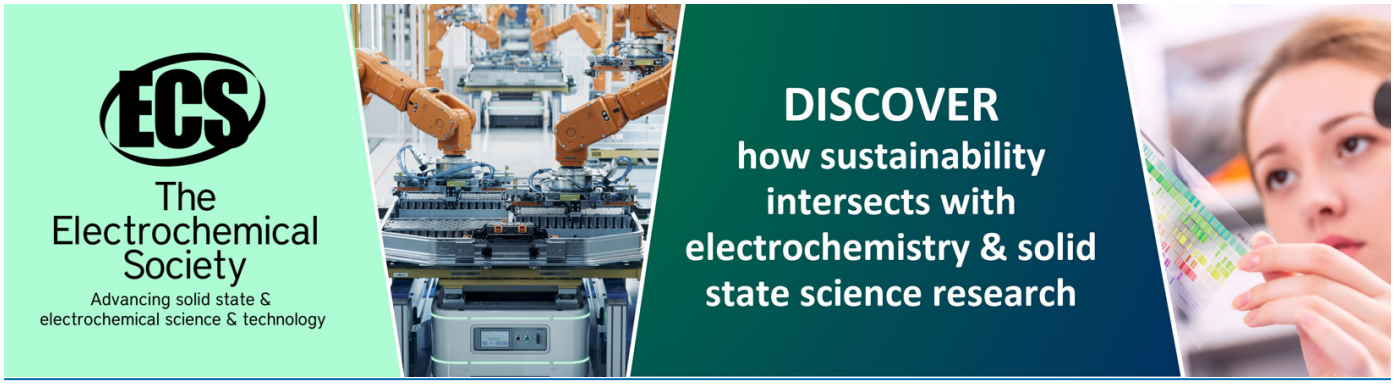

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XAFS study of the thermal behaviour of gold bulk and clusters

T Comaschi[1], A Balerna[2] and S Mobilio[1,2,3]

[1] Dip. di Fisica , Universit Roma Tre, via della Vasca Navale 84, 00146 Roma, Italy
[2] INFN-Laboratori Nazionali di Frascati, via E. Fermi 40, 00044 Frascati (Roma), Italy
[3] TASC-CNR Laboratory, Area Science Park, SS 14, Km 163.5, 34012 Trieste, Italy

E-mail: antonella.balerna@lnf.infn.it

Abstract. Materials showing negative thermal expansion (NTE) coefficient over large temperature ranges are nowadays of great interest for their possible applications. Small nanoparticles show changes in their properties with respect to the corresponding bulk, mainly due to the high surface to volume ratio and to the confinement of electrons in a small volume. In the present paper we report a x-ray absorption fine structure (XAFS) study on the thermal expansion coefficient of an Au foil and of Au nanoparticles of very small dimensions ranging from 2.4 nm and 5.0 nm. Their L_3 edge has been investigated in the temperature range 20K - 300K and a very accurate data analysis has been performed taking into account the presence of asymmetry effects. All clusters showed a thermal trend of the first shell distance significantly different from that of the bulk. The larger clusters were characterized by a reduction of the thermal expansion coefficient with respect to bulk; in the smallest samples the crossover from a thermal expansion to a NTE effect was observed. A simple model, based on the contribution of localized states induced by the finite size of the clusters, qualitatively accounts for the observed behaviour.

1. Introduction

Thermal expansion is one of the most direct measures of anharmonicity in molecules and solids [1]. Since the interatomic potential is generally asymmetric with respect to the potential minimum, the average interatomic distance depends on temperature and usually increases with temperature because of a looser barrier at longer distances. Effectively the idea of thermal expansion as purely due to the atomic vibrations, which increases the mean distance between atoms when they are thermally excited, is valid only for close-packed crystals which are practically elastically isotropic. This picture, in fact, is not adequate for systems in which transversal modes are present as in the case of interfaces and nanoparticles: their low coordination at the surface gives rise to an open structure, inducing changes also in the thermal expansion [2]. Macroscopic thermal expansion is generally considered the resulting effect of two different competing contributions, a positive one connected to bond stretching and a negative one associated to a sort of geometrical tension effect. This last contribution is connected to the vibrational motions perpendicular to the bond direction and induces a contraction of the interatomic distances. In some cases such a contraction can prevail giving rise to an overall negative thermal expansion (NTE) [3].

Recently temperature dependent x-ray diffraction measurements on gold nanoparticles with a mean dimension of about 4 nm showed for the first time an additional effect, i.e., the occurrence of a crossover in the temperature dependence of the cell parameter, which changes from an initial thermal expansion at low temperatures to a thermal contraction for T around 125 K [4]. This result is not due to changes in the structure of the nanoparticles, which continues to show a fcc atomic arrangement as the bulk metal but can be attributed to the contribution of electronic excitations to the total energy of the system: in nanoparticles, the presence of electronic discrete energy levels separated by only a few meV implies a relevant variation of the electronic energy with T. On the other hand for a bulk system, the electronic contribution to the total energy slowly varies with temperature and, for this reason, bulk materials generally show a thermal expansion, originating from the anharmonicity of the lattice potential. The aim of this paper is to show the results of a very accurate XAFS study on the thermal behavior of gold bulk [5] and nanoparticles [6] and explain the thermal effects found on nanoparticles using calculations based on the energy contribution of the electronic energy levels induced by the finite nanoparticle size.

2. Measurements and data analysis

X-ray absorption spectra, in transmission geometry, at the Au L_3 edge (11919 eV) and X-ray powder diffraction spectra at a fixed wavelength (0.68867 Å) were recorded at the BM08 GILDA beamline of the European Synchrotron Radiation Facility (ESRF) at Grenoble (France) [7]. Samples were a gold foil of 99.97% purity, 5 μm thickness and four nanoparticle samples (Au-NP1, Au-NP2, Au-NP3 and Au-NP4). Au-NP1 and Au-NP2 samples, supported on amorphous silica, were prepared [8, 9] using the SMAD technique and have respectively a mean particle size, D, of about 5 nm and 4 nm. Au-NP3 and Au-NP4 samples were produced on a 6 μm polymer film by consecutive evaporations of gold and Mylar [10] and their mean particle size, D, is of about 4.2 nm and 2.4 nm.

XAFS spectra were recorded in the temperature range from 20K up to 300K, using a liquid helium cryostat. The EXAFS (extended XAFS) spectra, $\chi(k)$, were extracted from the experimental X-ray absorption coefficient using standard procedures and the first coordination shells were analyzed [6] in two different ways [11, 12] using a phenomenological approach (ratio method) and a theoretical procedure (best-fit with amplitudes and phases calculated by the FEFF8 code [13]). In order to take into account asymmetry effects, whose importance increases with increasing temperature and with decreasing size, the cumulant expansion method [11] was used. X-ray powder diffraction measurements were taken at room temperature and the experimental data were analyzed [14] according to the Scherrer analysis of the diffraction peaks to obtain the cluster mean size of each nanoparticle sample.

3. Results and discussion

The x-ray absorption near edge structure (XANES) spectra, reported in Fig.1, clearly show that the typical fcc shape of Au bulk is present in the spectra of all the nanoparticle samples.

From the analysis of the first coordination shell data of the four nanoparticle samples at 20K, a contraction of interatomic distances (R), a reduction of coordination numbers (N) and an increase of structural disorder (σ^2) with decreasing size was found in agreement with previous studies Ref. [10, 15]. Lattice contraction is expected to occur in finite-size systems due to surface stress, according to the Laplace law:

$$\Delta R = -\frac{4}{3} K_B R_B f \frac{1}{D}. \quad (1)$$

where K_B is the bulk compressibility, R_B the bulk nearest-neighbor distance, f surface stress and D the mean cluster diameter. Quantitatively the values found for N and ΔR are in good agreement with those expected according to the nanoparticles size. The decrease of N is related

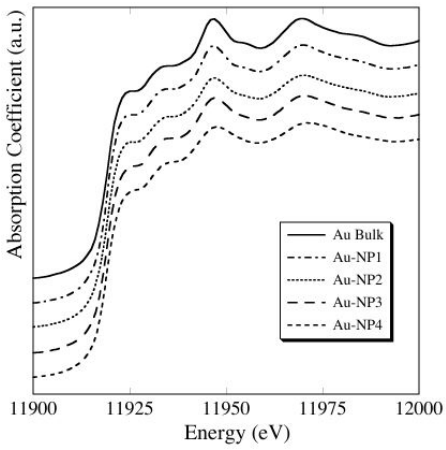

Figure 1. XANES spectra of Au bulk and of the four nanoparticles samples.

to the reduction of the mean coordination of the atoms inside the cluster due to the higher percentage of surface atoms with decreasing cluster size. Correspondingly also an enhancement of the structural disorder is expected as a consequence of higher asymmetry effects connected to the finite dimension of the systems and of the higher mobility of the surface atoms. An accurate data treatment was performed [6] also for the temperature dependence of the structural parameters of the first coordination shells. Using the thermal behavior of the EXAFS Debye-Waller factors found, well approximated by a Debye correlated model [15], a decrease of the Debye temperature, due to the mean higher mobility of the atoms of the cluster with respect to the bulk ones, was observed. Also the relative variations with respect to the data at 20 K of the mean interatomic distances as a function of T for the first coordination shell of the different samples has been investigated [15] and quite marked differences between the different samples and Au bulk were found. Au-NP1, the sample with the greatest nanoparticles size, has a bulk-like behavior showing a thermal expansion at all T but with a reduced value of the thermal expansion coefficient. Au-NP2, instead, at low T expands like the bulk; over 170K, its behavior changes showing a thermal contraction up to room temperature. Au-NP3 shows a reduced thermal expansion as found for Au-NP1 while Au-NP4 shows, quite clearly, a crossover effect from positive to negative expansion around 200K (Fig. 2).

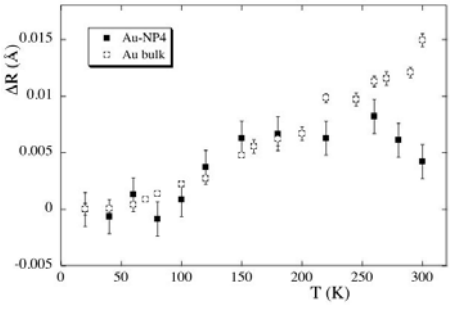

Figure 2. Relative variations as a function of T of the first cumulant of the real distribution for the first shell of the Au-NP4 sample compared to gold bulk ones.

In agreement with XRD results [4] the occurrence of negative thermal expansion effects were observed in some of the investigated samples; the presence of a negative thermal expansion in gold clusters was interpreted [6] as due to the presence of discrete electronic energy levels induced by the finite size of the nanoparticle. In order to have a complete understanding of the thermal behavior of our samples, the thermal behavior of the near-neighbor distance for approximately spherical gold nanoclusters of different sizes was calculated [6] from the total energy of the system taken as the sum of three main contributions: the static, the vibrational

and electronic energy of the particle respectively. The total energy of the nanoparticles was calculated as a function of their radius at each temperature. In this way the theoretical trends of the near neighbor distance as a function of T for some nominal sizes, was achieved (Fig. 3).

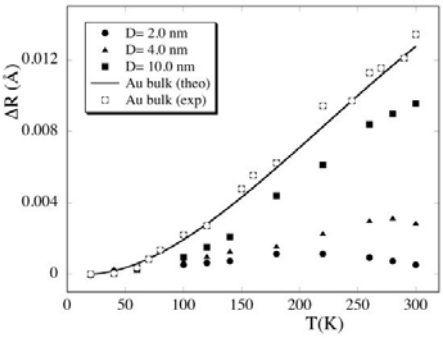

Figure 3. Comparison between the experimental Au bulk thermal expansion values and the theoretical ones found for a bulk-like system together with the theoretical trends for different nanoparticle dimensions.

The different thermal behaviors found, in quite good agreement with the experimental results, are originated by the different balance between the vibrational energy (leading to positive expansion with increasing T) and the electronic energy (leading to negative thermal expansion), which changes with changing the size of the system.

4. Conclusions

An EXAFS study of four Au nanoparticles samples and of an Au foil has been performed in the temperature range from 20K to 300K. Results achieved exclude the presence of a structural phase transition at any T for each cluster dimension. An accurate analysis was performed for the first coordination shell in order to see how the thermal behavior of such confined objects changes with decreasing their size. For all the nanoparticles the temperature dependence of the first shell interatomic distances found was different from the corresponding macrocrystalline counterpart. Their behaviors are in quite good agreement with calculations based on the energy contribution of the electronic energy levels induced by the finite clusters size.

4.1. Acknowledgments

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