

# Laboratori Nazionali di Frascati

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THE DETERMINATION OF THE DYNAMICAL PROPERTIES OF SMALL  
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A NEW FORMULATION OF THE EXAFS DEBYE-WALLER FACTOR FOR THE DETERMINATION OF THE DYNAMICAL PROPERTIES OF SMALL GOLD CLUSTERS

A.Balerna and S.Mobilio

INFN, Laboratori Nazionali di Frascati, 00044 Frascati, Italy

In previous EXAFS studies<sup>(1,2)</sup> we investigated the structural peculiarities of evaporated small gold clusters with a mean diameter ranging from 11 Å up to 42.5 Å. The presence of contractions in the interatomic distances, the lowering of the mean coordination number and increasing Debye-Waller (DW) factors with decreasing cluster size were found. No structural changes from the bulk fcc structure to the icosahedral structure, theoretically predicted, were revealed.

At that time we interpret the behaviour of the cluster DW factors in terms of a lowering of the Debye temperature ( $\theta_D$ ) of the clusters with respect to the bulk one.

Such interpretation, anyway, gives Debye temperature values which do not agree with the values predicted within the free bounded sphere model (Fig. 1).

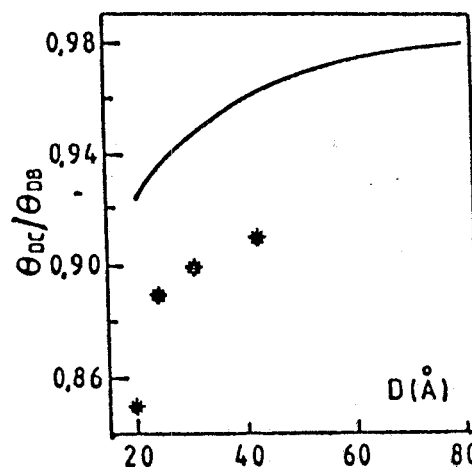


Fig. 1 - Plot of the ratio  $\theta_D^{\text{CLUSTER}} / \theta_D^{\text{BULK}}$  as a function of the cluster mean diameter. The solid line represents the theoretical behaviour obtained from ref.(5), the (\*) are the experimental values.

Before trying to understand such a mismatch, we checked the possibility to obtain a reliable  $\theta_D$  from an EXAFS data set. Indeed it is known that the  $\theta_D$  is not a well defined physical parameter of a system but it varies depending on the physical quantity (heat capacity, thermal expansion factor, root mean square atomic displacement) used to determine it.

Fig. 2 shows the behaviour of the theoretical EXAFS DW factor for Au bulk as a function of the temperature, evaluated in the Debye approximation using the Beni and Platzmann<sup>(3)</sup> formula, together with the experimental values. The  $\theta_D$  value (165 K) (Fig. 2) is in good agreement with the one given by heat capacity measurements, thus confirming that a correct bulk  $\theta_D$  is obtainable from EXAFS data.

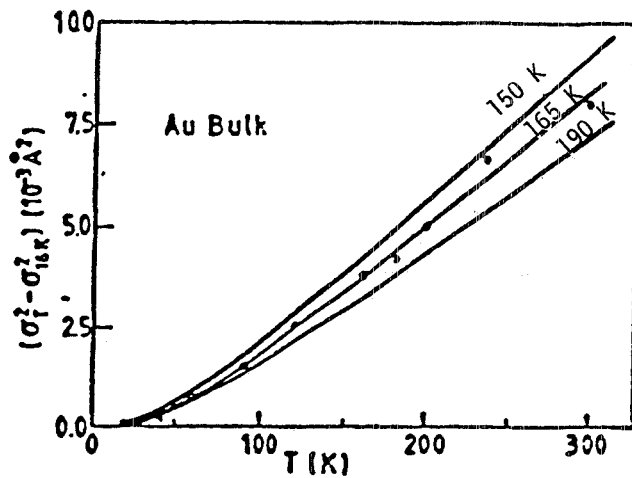


Fig. 2 - A comparison between the theoretical gold bulk Debye-Waller factor evaluated for several temperatures (solid line) and the experimental values (dots).

The mismatch shown in Fig. 1 is due to an incorrect use of the Beni and Platzmann formula, since it takes into account only the bulk modes and not also the surface ones which become more and more important in small clusters whose surface to volume ratio is very high.

Moreover in a cluster of linear dimension  $D$ , phonon modes whose wave-vector is shorter than  $q_{\min} = \pi/D$  cannot be excited. This changes also the normalization condition which has to be integrated not from zero but from a finite value  $\omega_{\min} = v_s \pi/D$  up to  $\omega_{\max}$ .

<sup>(4)</sup> For this reason we evaluated the cluster DW factors with a new formula which takes into account these two points.

An excellent agreement between the cluster theoretical and experimental DW factors has been found (Fig. 3). It follows that the dynamical pro-

properties of gold clusters are well described by the free bounded sphere density of states in a Debye approximation. This gives also a strong support to the macroscopic sphere model which can fully explain the structural and dynamical properties for our small gold clusters.

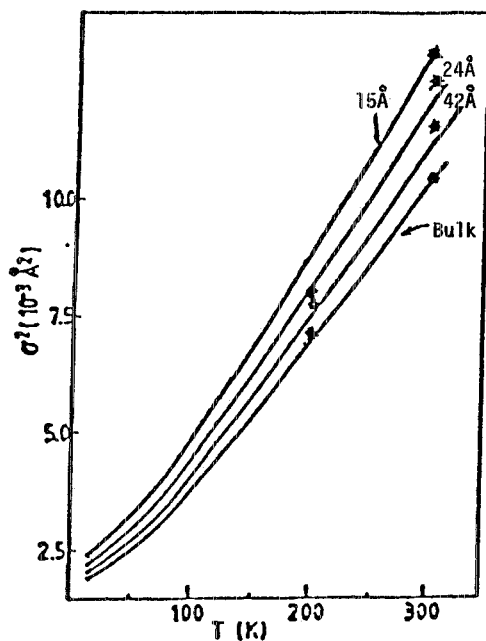


Fig. 3 - A comparison between the theoretical behaviour of the EXAFS cluster Debye-Waller factors for different cluster diameter (solid line) and the experimental values (\*).

References:

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