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NOBLE METAL SMALL CLUSTER EXAFS

Estratto da:
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1. Introduction

Many experimental and theoretical works (1) have been and are being performed on the structural properties of small metal clusters in order to investigate possible differences from the corresponding bulk metal structure. Attention is generally devoted to the following points: 1) if there is or not a contraction in the lattice parameter with decreasing cluster size; 2) if there is or not a structural transition from the bulk crystallographic structure to icosahedron which should be for thermodynamical and dense packing considerations the most stable structure for a few atoms system.

From an experimental point of view the answer to the first question seems to be dependent on the clusters preparation method and on the interactions with the substrates. Metal clusters supported on weakly interacting substrates and prepared using physical methods, like thermal evaporation, generally show a contracted lattice parameter though there are large discrepancies on the numerical values found for the contractions. On the other hand, chemically prepared clusters, like reduced supported catalysts, never show appreciable contractions. Therefore great attention must be given to fully understand the physical origin of such different behaviours.

With regard to the structural changes, no definite evidence has been found to ascertain or exclude experimentally the occurrence of the icosahedral structure for small metal clusters.

This work reports an EXAFS structural characterization of evaporated Au metal clusters supported on a weakly interacting substrate, like mylar, in order to study the cluster intrinsic structural properties. The presence of lattice parameter contractions, the non existence of icosahedron-like structure and the decrease of the cluster Debye temperature due to the softening of the phonon spectrum are the main results here reported.

2. Experimental

Samples were prepared in vacuum, by evaporating on a 6 μm mylar film multiple layers of gold and mylar until the optimum metal thickness for X-ray measurements was achieved.

Gold and mylar depositions were both controlled with a quartz-crystal detector. Discontinuity of the multilayer samples has been checked with optical transmission measurements (2). Cluster size distributions were obtained using electron microscopy analysis. Their mean diameter ranges from 11 Å to 50 Å.

The X-ray absorption spectra have been recorded on the Au L₂,3 edge at both liquid nitrogen temperature (LNT) and room temperature (RT). Measurements have been done at the Frascati National Synchrotron Radiation Laboratory using the wiggler beam line, whose monochromator was equipped with a Si(111) channel-cut crystal.

3. Results and discussion

The X-ray absorption spectra have been analyzed using a standard procedure (3) in order to obtain the values of the interatomic distances (R₁), the mean coordination
Table 1. EXAFS results obtained using k-space analysis for the first and second coordination shells. Gold bulk was used as reference compound. The Debye-Waller factors are the total values. Values for gold bulk were obtained from Ref.4.

<table>
<thead>
<tr>
<th>D(Å)</th>
<th>R₁(Å)</th>
<th>R₂(Å)</th>
<th>R₂/R₁</th>
<th>N</th>
<th>σ²ₓ²(R₁)(Å²)</th>
<th>σ²_LNT(R₂)(Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.5</td>
<td>2.88</td>
<td>4.07</td>
<td>1.41</td>
<td>12.0</td>
<td>4.9×10⁻³</td>
<td>1.7×10⁻³</td>
</tr>
<tr>
<td>30.0</td>
<td>2.86</td>
<td>4.03</td>
<td>1.41</td>
<td>11.0</td>
<td>6.7×10⁻³</td>
<td>2.4×10⁻³</td>
</tr>
<tr>
<td>24.0</td>
<td>2.85</td>
<td>4.03</td>
<td>1.41</td>
<td>10.6</td>
<td>7.0×10⁻³</td>
<td>2.6×10⁻³</td>
</tr>
<tr>
<td>20.0</td>
<td>2.83</td>
<td>4.01</td>
<td>1.42</td>
<td>9.6</td>
<td>8.6×10⁻³</td>
<td>4.2×10⁻³</td>
</tr>
<tr>
<td>15.0</td>
<td>2.82</td>
<td>3.99</td>
<td>1.42</td>
<td>9.4</td>
<td>10.7×10⁻³</td>
<td>5.3×10⁻³</td>
</tr>
<tr>
<td>11.0</td>
<td>2.81</td>
<td>3.95</td>
<td>1.41</td>
<td>---</td>
<td>10.0×10⁻³</td>
<td>---</td>
</tr>
</tbody>
</table>

* Numbers (N) and the Debye-Waller factors (σ²) for the first shells and the interatomic distances (R₂) for the second coordination shells (Table 1).

It can be seen in Fig. 1 that as the cluster size decreases there is a decrease of the interatomic distances of both the first and second coordination shells. These contractions are due to the comprehensive force exerted by the surface stress on the small good clusters. Using a macroscopic liquid drop model, the contractions can be described by the relation:

$$\Delta R = -\frac{4}{3} K R_b f \frac{1}{D}$$  \hspace{1cm} (1)

Fig. 1a. Fourier transform of some films and bulk EXAFS spectra relative to the first coordination shell. The transformations have been performed in the k range 3-11 Å⁻¹ using a gaussian window and a k weight.

Fig. 1b. Fourier transform of some films and bulk EXAFS spectra relative to the second coordination shell using the same conditions of Fig. 1a.
where $f$ is the surface stress, $K$ is the bulk compressibility, $R_b$ is the metal bulk interatomic distance and $D$ is the cluster mean diameter. A good agreement between this model and the experimental data is shown by the linear behaviour reported in Fig. 2.

Great attention was given to the possible presence of asymmetry effects in the radial distribution function, which can result in apparent nearest-neighbour contractions (5,6). The origin of such effects can be dynamical or static. Dynamical asymmetry effects can be excluded because the cluster total phase, obtained by EXAFS data analysis, was found to be independent from temperature. On the other hand the presence of asymmetry static effects can be excluded "a posteriori" since the analysis with a gaussian function gives results for $R$, $N$ and $\sigma^2$ which are completely explained by the increase surface to volume ratio. Moreover the good agreement between our data and the ones obtained using electron diffraction (7,8) excludes further the presence of asymmetry effects.

From Table I it can be seen that the ratio $R'/R_1$ is for all samples equal to $\sqrt{2}$ as expected for an fcc structure; it is thus possible to exclude changes from the fcc structure to the icosahedron one also for the 11 Å clusters. In order to exclude this further on, the first shell EXAFS data were fitted using a single shell model (fcc-like structure) and a double shell model. In the icosahedron, in fact, the first fcc shell is split in two shells centered at distances $R$ and $R'$ related by:

$$R' = 1.056 \ R.$$ 

Good fits were obtained using only an fcc-like model. This result disagrees with the thermodynamical calculations which predict that the icosahedral structure is the most stable for clusters containing less than 150 atoms ($D < 15 \ \text{Å}$). It must be underlined that the calculated energy difference between the fcc and the icosahedral structure is only about 0.02 eV/atom (9). We think that for this reason it is not possible to neglect contributions to the interatomic potential, given by larger effects like the shift of the clusters $5f$-band of the order of $\sim 1$ eV (10).

Coordination numbers reported in Table I show a decrease with decreasing clusters size due to the increased number of surface atoms respect to the bulk ones. Values obtained are in agreement with the ones calculated by Mason (10) using highly symmetrical geometries.

Debye-Waller factors evaluated at RT and at LNT increase as the cluster size decreases. This increase in cluster disorder is mainly dynamical in origin due to the increased surface to volume ratio and to the higher mobility of the surface atoms. As reported in Ref. (2), using the Debye approximation it is possible to calculate the clusters Debye temperatures, $\Theta_D$ (Table II).

The decrease in clusters Debye temperatures is due to the higher mobility of the surface atoms with respect to the bulk. LEED measurements determined gold surface Debye tem-
Table II. Debye temperatures for some of the samples studied.

<table>
<thead>
<tr>
<th>D(Å)</th>
<th>θ₇₅(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.5</td>
<td>150</td>
</tr>
<tr>
<td>30.0</td>
<td>148</td>
</tr>
<tr>
<td>24.0</td>
<td>148</td>
</tr>
<tr>
<td>20.0</td>
<td>140</td>
</tr>
</tbody>
</table>

Temperatures for the different Miller planes: such temperatures are lower than the bulk one (11). Assuming that the clusters Debye temperatures approach the surface one averaged on all the possible surface planes, we obtained for gold:

\[ \theta_D^\text{cluster} = 135 \text{ K} \approx 0.8 \theta_D^\text{bulk} \]

in good agreement with data reported in Table II.

This work clearly shows that for gold clusters non-interacting with the substrate, there is a real presence of contractions in the lattice parameters and there are no structural transitions from the bulk fcc structure to icosahedron. Attention will be given in the future to the structural behaviour of gold clusters using different substrates and preparation methods.

References