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DYNAMIC PROPERTIES AND DEBYE TEMPERATURES OF BULK AU AND AU CLUSTERS STUDIED USING EXTENDED X-RAY-ABSORPTION FINE-STRUCTURE SPECTROSCOPY

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Dynamic properties and Debye temperatures of bulk Au and Au clusters studied using extended x-ray-absorption fine-structure spectroscopy

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The L_3 edge of bulk Au has been studied using x-ray-absorption spectroscopy in the temperature range 16—300 K. An effective Debye temperature of 165 K is derived from the thermal behavior of the extended x-ray absorption fine-structure Debye-Waller factors. Their behavior is also calculated for finite systems by using a free-bounded-sphere density of states and a Debye approximation for the phonon spectra. An excellent agreement is found with experimental data previously reported on Au clusters with mean diameters ranging from 15 to 43 Å. This confirms that the dynamic properties of Au clusters are well described by a liquid-drop model in agreement with heat-capacity measurements.

I. INTRODUCTION

In previously written papers,[1,2] a complete structural characterization of vacuum-evaporated gold clusters supported on Mylar has been reported using extended x-ray-absorption fine-structure spectroscopy (EXAFS).[3,4] The behavior of nearest-neighbor (NN) and next-nearest-neighbor (NNN) distance contractions as a function of the cluster diameter was fully explained by a simple macroscopic liquid-drop model: clusters are imagined as homogeneous spheres on which surface stress acts, shortening the lattice parameter with respect to the bulk one. The increased atomic mean-square displacement found from EXAFS data was qualitatively interpreted in the sphere model as being due to the increased number of surface atoms with respect to the volume.

Such a macroscopic free-sphere model has been successfully used to explain many other properties of small metal clusters[5] such as the low-temperature specific-heat behavior,[6,9] the lowering of the melting temperature,[10] and the mean-square atomic displacement.[11,12] Indeed these properties, because of softening of lattice vibrations, can be quantitatively calculated by assuming for the cluster phonons the free-bounded-sphere density of states.[6]

The change of cluster phonon spectrum can also be described in terms of a change in the Debye temperature ($\Theta_D^{\text{cluster}}$)[13–15] but only when it is possible to unambiguously determine $\Theta_D^{\text{cluster}}$. In order to do this, it is clear that the first step must be to correctly determine bulk Θ_D. For this reason, in this paper we report the L_3 x-ray-absorption spectra of gold in the temperature range 16—300 K. From these data we show that it is possible to get an accurate measure of the Debye temperature, Θ_D, from EXAFS. Nevertheless, it will be shown that the peculiar dynamical properties of gold clusters, as measured from EXAFS Debye-Waller factors, cannot be described simply assuming a decrease in Θ_D as the cluster size decreases. On the other hand, a complete calculation using the free-bounded-sphere density of state (DOS) gives the EXAFS Debye-Waller factors, for the clusters in good agreement with the experimental values.

The layout of this paper is as follows: Sec. II describes the experimental measurements performed on gold bulk metal at several temperatures and the EXAFS data handling used to extract the σ^2 values; Sec. III describes the results obtained on Θ_D for the bulk and for the clusters and the calculations of the clusters σ^2 together with a discussion on the results; Sec. IV is a summary of the main results.

II. X-RAY-ABSORPTION MEASUREMENTS

X-ray-absorption spectra (Fig. 1) were recorded in the temperature range 16—300 K at the Frascati Synchrotron

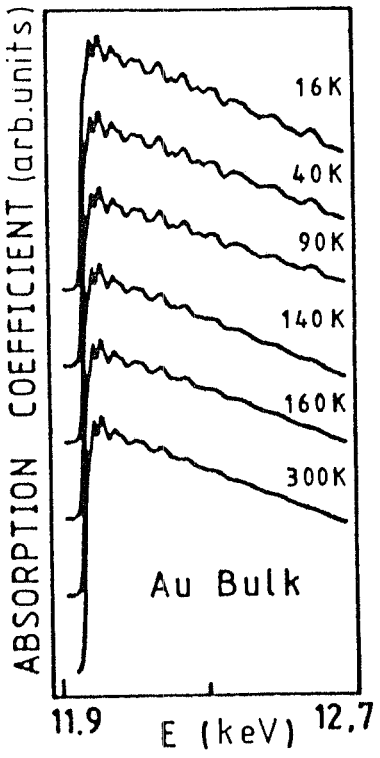

FIG. 1. Gold L_3 absorption spectra at different temperatures.

Radiation facility using the bending-magnet beam line with typically $I=40$ mA and $E=1.5$ GeV in the storage ring. The x-ray beam was monochromatized by a Si(111) asymmetric channel-cut crystal and the detection of the x-ray beam was achieved by two Ar-filled ionization chambers. The average photon flux was $\approx 10^9$ photons/s and the resolution was ≈ 2 eV. The sample was cooled and its temperature stabilized by an Air Liquid variable-temperature cryostat.

A. EXAFS results and analysis

The x-ray-absorption spectra were analyzed using a standard procedure[16] already described. To obtain the normalized EXAFS spectra, we fitted the curve of $\ln(I_0/I)$ above the edge with a polynomial, thus obtaining the oscillations around the smooth background $(\mu-\mu_0)d$. The EXAFS spectrum or $\chi(k)$ was defined as

$$\chi(k)=(\mu-\mu_0)d/\mu_0 d ,$$

assuming for $\mu_0 d$, $\mu_0 d=J[1-(8/3)k^2a^2]$, where $a=\hbar/(2mE_0)^{1/2}$. E_0 is the energy of the edge, k is the photoelectron wave vector given by $k=[2m(E-E_0)/\hbar^2]^{1/2}$ and J is the jump in $\ln(I_0/I)$ at the edge.[17] Figures 2 and 3 shows the EXAFS spectra and their Fourier transform (FT), respectively.

The analysis of the NN peak was performed in the k space by backtransforming the first FT peak (Fig. 3). First-neighbor coordination numbers and the Debye-Waller factors σ^2, were obtained from the usual plot of $\ln[A_S(k)/A_M(k)]$ versus k^2,[18] $A_S(k)$ and $A_M(k)$ being the amplitude of the inverse FT of the sample and of the reference compound, respectively. The $T=16$ K measurement was used as the reference. Table I reports the coordination numbers and the Debye-Waller factors obtained.

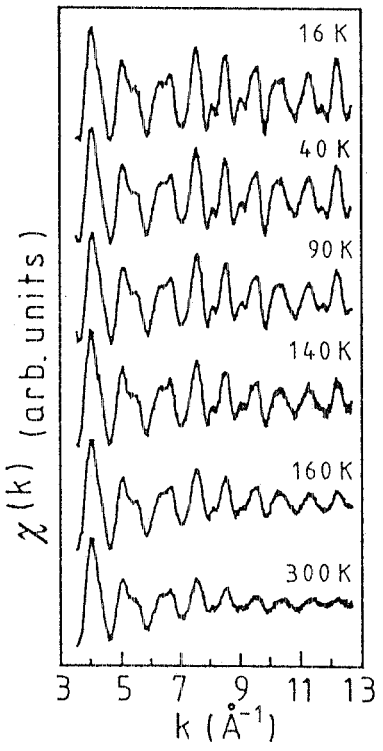

FIG. 2. Gold bulk EXAFS spectra at different temperatures.

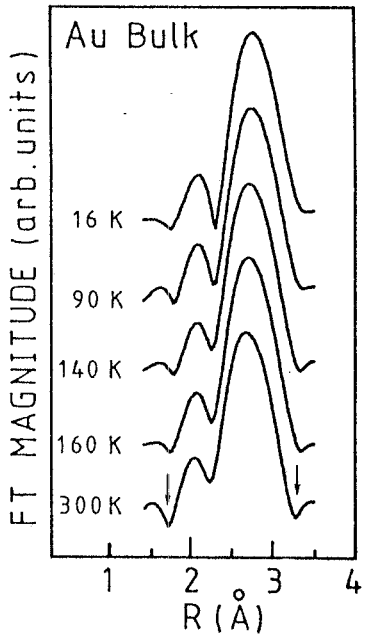

FIG. 3. Gold Fourier transform (FT) at different temperatures. The FT were performed in the range 3–13 Å^{-1}, with a Gaussian window function and a k^1 weight. The arrow shows the R range used to get the inverse FT.

III. EXAFS AND DEBYE TEMPERATURES

It has been pointed out many times[19,20] that the Debye temperature is not a well-defined physical parameter of a system. Its definition is a mathematical condition for the normalization of the phonon DOS: $\int_0^{\omega_D} D(\omega)d\omega=3N$, in the hypothesis of a linear dispersion relation. Each phonon-dependent physical parameter like the heat capacity, the Grüneisen constant, the thermal expansion, and the root-mean-square atomic displacement can be described in terms of such a continuum Debye model and used to evaluate Θ_D. But from each physical parameter, one gets an effective Debye temperature: indeed each parameter depends on the true DOS properly weighted on

TABLE I. Coordination numbers and Debye-Waller factors for the first shell of gold bulk as a function of temperature.

T (K)	N	$\sigma^2_T-\sigma^2_{16\,K}$ (10^{-3} Å^2)
16	12	0.00
40	11.9	0.20
60	11.6	0.75
90	12	1.50
105	11.9	2.20
120	12.3	2.60
160	11.7	3.80
180	11.9	4.10
200	12.2	5.00
235	11.3	6.70
300	12.3	7.90

the Brillouin zone, the weighting factor being specific to it. So any deviation of the true DOS from the Debye DOS can result in a different effect on Θ_D.

The Θ_D evaluated from x-ray diffraction are typically $\approx 5\%$ (Ref. 19) lower than those evaluated from heat capacity, while it is not clear at all which value is obtainable by EXAFS, since few cases have been studied in detail.[21–27] For this reason, we used gold EXAFS data to evaluate its EXAFS Θ_D.

Beni and Platzmann[21] showed that, whereas the temperature behavior of the x-ray diffraction pattern depends on the total-mean-square displacement of a given type of atom, the relevant quantity in the EXAFS amplitude is the mean-square relative displacement (MSRD) of the central atom relative to its neighbors (σ^2_{BP}). They calculated that the thermal contribution to the disorder is given by

$$\sigma^2_{BP}(T)=2\sigma^2_{\text{x-ray}}-2\sigma^2_{\text{corr}} , \tag{1}$$

with

$$\sigma^2_{\text{x-ray}}(T)=(3\hbar^2/Mk_B\Theta_D)[(\tfrac{1}{4})+(T/\Theta_D)^2]\int_0^{x_D} x/[\exp(x)-1]dx , \tag{2}$$

$$\sigma^2_{\text{corr}}(T)=(3\hbar^2/Mk_B\Theta_D)\left\{[1-\cos(q_DR_j)]/\cos(q_DR_j)+(T/\Theta_D)^2\int_0^{x_D}[\sin(\Omega x)/\Omega]/[\exp(x)-1]dx\right\} . \tag{3}$$

In this expression, $\sigma^2_{\text{x-ray}}$ and σ^2_{corr} are the total and correlated atomic root-mean-square displacements, respectively, Θ_D, q_D are the Debye temperature and wave vector, M is the atomic mass, k_B is the Boltzmann constant, T is the absolute temperature, and $\hbar$ is Planck's constant. x is defined as $\hbar\omega/k_BT$ and Ω as q_DR_j/x_D.

The meaning of Eq. (1) is that, if the central atom and its neighbors move the same amount in the same direction (correlated phonon), the relative distance between them does not change and so such a phonon does not contribute to MSRD.

Figure 4 shows the behavior of σ^2_{BP} calculated from Eq. (1) for several Θ_D. A good agreement with experimental data is found for $\Theta_D=165$ K. Such a value is in excellent agreement with 162 and 165 K, obtained from the normalization condition and from heat-capacity measurements[28–29] but is considerably lower than 190 K, obtained from thermal expansion measurements.[30]

This result shows that in bulk gold metal, an accurate measurement of Θ_D can be performed by examining the thermal behavior of the amplitude of the EXAFS spectra at low temperatures.

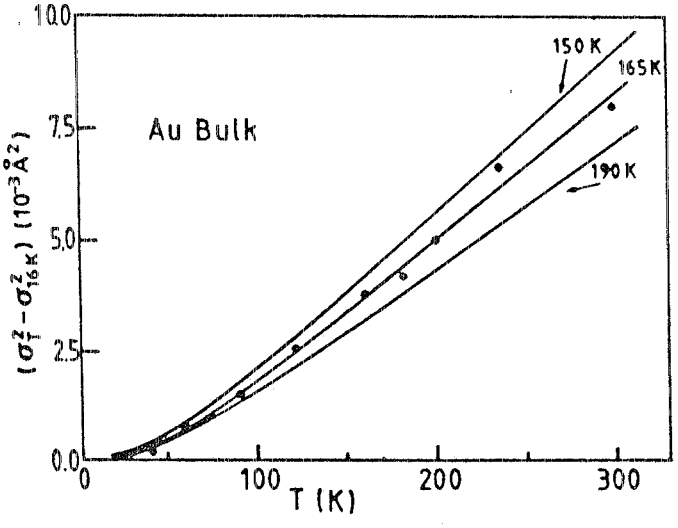

FIG. 4. A comparison between the theoretical gold Debye-Waller factor evaluated for several temperatures and the experimental data of Table I.

A. Gold-cluster Debye temperatures

In Refs. 1 and 2, we reported the dynamical Debye-Waller factors and the Debye temperatures for gold clusters in the diameter range 15—43 Å (Table II) and concluded that the increase of the former is essentially due to decreasing $\Theta_D^{\text{cluster}}$. From a qualitative point of view, the decrease of the Debye temperature with decreasing cluster diameter is easily understood as being due to the great number of surface atoms: surface atoms indeed have a higher mobility than the bulk ones;[31] so an EXAFS measurement which averages the behavior of each atom in the sample must detect a higher mean atomic mobility.

More puzzling is the numerical understanding of data in Table II. Baltes and Hilf[6] showed that for a free-bounded sphere, the phonon DOS is well approximated by

$$N(k)dk=(2/3\pi)R^3k^2+(\tfrac{1}{2})R^2k+(2/3\pi)R , \tag{4}$$

where the three terms are due to the volume, surface, and line modes. Using Eq. (4), Chouchman and Karasz[15] calculated the ratio $\Theta_D^{\text{cluster}}/\Theta_D^{\text{bulk}}$ as a function of the cluster dimensions. Their values are plotted in Fig. 5 together with the experimental data of Table II. The evident numerical disagreement is enhanced by an effect neglected in Ref. 15. Indeed, in a finite volume of linear dimension D phonon modes whose wave vector is shorter than

TABLE II. Values of dynamical σ^2 for clusters at different temperatures obtained from Ref. 1. The absolute values have been obtained assuming σ^2_{bulk} (200 K) as reference compound, equal to 7.12×10^{-3} Å^2.

D (Å)	$\sigma^2_{200\text{ K}}$ (10^{-3} Å^2)	$\sigma^2_{300\text{ K}}$ (10^{-3} Å^2)	$\Theta_D^{\text{cluster}}\Theta_D^{\text{bulk}}$
15		13.2	
20	8.70	13.9	0.85
24	8.10	12.5	0.89
30	8.00	12.4	0.90
93	7.82	11.1	0.91

$q_{min}=\pi/D$, cannot be excited. As a consequence, the normalization condition has to be integrated from value $\omega_{min}=v_s\pi/D$ up to $\omega_D^{cluster}$. Such an effect for a definite sphere diameter will increase the upper limit of integration thereby increasing the $\Theta_D^{cluster}/\Theta_D^{bulk}$ ratio.

We believe that the disagreement observed between our experimental data and the calculated data comes from the method used in Ref. 1 to evaluate $\Theta_D^{cluster}$ from the experimental data. Indeed, the asymptotic expansion of Eq. (1) for $T/\Theta_D \gg 1$ was used:

$$\sigma^2_{cluster}\approx(6\hbar^2/Mk_B\Theta_D)0.65[\tfrac{1}{4}+(T/\Theta_D)^2D_1]\ , \qquad (5)$$

where

$$D_1=\int_0^{\Theta_D/T} x/[\exp(x)-1]dx\approx\Theta_D/T\ .$$

In this asymptotic expression, the factor 0.65 comes from the behavior of the correlation factor $\sigma^2_{corr}/\sigma^2_{x\text{-}ray}$ which, for $T/\Theta_D\gg1$, reaches the asymptotic value of 0.35.[21]

The approximated Eq. (5) is not valid for clusters since (1) the total surface-mode contribution to MSRD cannot be neglected with respect to the bulk contribution and (2) the correlation factor changes in clusters with respect to the bulk, so it is not possible to assume *a priori* the value 0.35 for it. In order to give a quantitative evaluation of these effects we calculated the behavior of σ^2 in clusters using the total DOS of the sphere model.[6] For this purpose we have developed an extension of the Beni-Platzmann formula which applies to finite systems, therefore also to metallic clusters.

B. Thermal behavior of EXAFS spectra

The MSRD of a pair of atoms j and j' is given by[21]

$$\sigma^2_{jj'}=\langle\,|(\mathbf{u}_j-\mathbf{u}_{j'})\cdot\hat{\mathbf{R}}_j|^2\rangle$$

$$=2\langle(\mathbf{u}_j\cdot\hat{\mathbf{R}}_j)^2\rangle-2\langle(\mathbf{u}_j\cdot\hat{\mathbf{R}}_j)(\mathbf{u}_{j'}\cdot\hat{\mathbf{R}}_j)\rangle\ ,$$

$\mathbf{u}_j,\mathbf{u}_{j'}$ being the thermal displacements of the atoms j and j', $\hat{\mathbf{R}}_j$ the unit vector in the direction connecting the atoms j and j' a distance R_j apart, and $\langle\cdots\rangle$ the thermal average.

For a randomly oriented system and three identical polarizations, $\sigma^2_{jj'}(T)$ becomes

$$\sigma^2_{jj'}(T)=(2/NM)\int_{\omega_{min}}^{\omega_{max}}[D(\omega)/\omega^2]\{\hbar\omega/2+\hbar\omega/[\exp(\hbar\omega/k_BT)-1]\}d\omega$$
$$\times\left\{-(2/NM)\int_{\omega_{min}}^{\omega_{max}}[D(\omega)/\omega^2][\sin(qR_j)/qR_j]\{\hbar\omega/2+\hbar\omega/[\exp(\hbar\omega/k_BT)-1]\}d\omega\right\}\ , \qquad (6)$$

N being the total number of atoms in the system. The integrations are performed from the minimum up to the maximum frequency allowed in the sample. For the bulk $\omega_{min}=0$, $\omega_{max}=\omega_D$, $D(\omega)=3N\omega^2/\omega_D^3$, so Eq. (6) becomes the usual Beni and Platzmann formula.

To calculate the cluster σ^2, we assumed to be valid, for

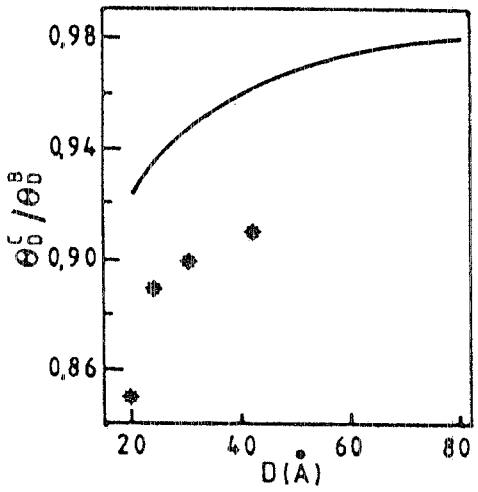

FIG. 5. Plot of the ratio $\Theta_D^{cluster}/\Theta_D^{bulk}$ as a function of the cluster mean diameter. The solid line represents the theoretical behavior obtained from Ref. 15; asterisks are the experimental values reported in Table II.

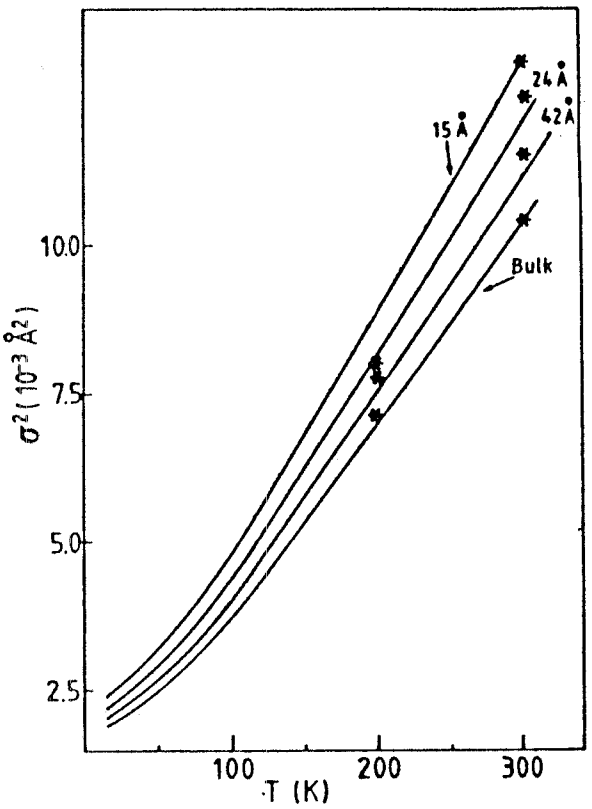

FIG. 6. Comparison between the theoretical behavior of the EXAFS cluster Debye-Waller factors for different cluster diameter (solid line) and the experimental values of Table II (*).

the cluster phonon spectrum, Eq. (4), which is valid for an homogeneous sphere. The integrations were performed from $\omega_{\min}$ corresponding to $q_{\min}=\pi/D$ up to $\omega_{\max}$ corresponding to $q_{\max}$ defined by the normalization condition:

$$3N=(2/9\pi)R^3(q_{\max}^3-q_{\min}^3)+R^2/4(q_{\max}^2-q_{\min}^2)+(2/3\pi)(q_{\max}-q_{\min}) . \quad (7)$$

In such a way, σ^2 for a cluster becomes

$$\sigma_{jj'}^2(T)=2[(\sigma_{\text{x-ray}}^V)^2-(\sigma_{\text{corr}}^V)^2]+2[(\sigma_{\text{x-ray}}^S)^2-(\sigma_{\text{corr}}^S)^2] , \quad (8)$$

where the symbols V and S refer to the volume and surface contributions, respectively. The line mode has been neglected according to Ref. 15. The single contributions are given by

$$(\sigma_{\text{x-ray}}^V)^2=(3\hbar^2/Mk_B\Theta_D)(N_A^{\text{bulk}}/N_A^{\text{sphere}})\left[(q_{\max}^2-q_{\min}^2)/4q_D^2+(T/\Theta_D)^2\int_{x_{\min}}^{x_{\max}}x/[\exp(x)-1]dx\right] ,$$

$$(\sigma_{\text{corr}}^V)^2=(3\hbar^2/Mk_B\Theta_D)(N_A^{\text{bulk}}/N_A^{\text{sphere}})\left[[\cos(q_{\min}R_j)-\cos(q_{\max}R_j)]/2(q_DR_j)^2+(T/\Theta_D)^2\int_{x_{\min}}^{x_{\max}}[\sin(\Omega x)/\Omega]/[\exp(x)-1]dx\right] ,$$

$$(\sigma_{\text{x-ray}}^S)^2=(3\hbar^2/Mk_B\Theta_D)(N_A^{\text{bulk}}/N_A^{\text{sphere}})(S/V)(\pi/4q_D)\left[(q_{\max}-q_{\min})/2q_D+(T/\Theta_D)\int_{x_{\min}}^{x_{\max}}1/[\exp(x)-1]dx\right] ,$$

$$(\sigma_{\text{corr}}^S)^2=(3\hbar^2/Mk_B\Theta_D)(N_A^{\text{bulk}}/N_A^{\text{sphere}})(S/V)(\pi/4q_D)\left[(1/2q_DR_j)\int_{q_{\min}R_j}^{q_{\max}R_j}\sin(qR_j)/(qR_j)d(qR_j)+(T/\Theta_D)\int_{x_{\min}}^{x_{\max}}[\sin(\Omega x)/\Omega x]/[\exp(x)-1)]dx\right] .$$

N_A^{bulk} and N_A^{sphere} being the number of atoms per unit volume in the bulk and in the cluster, S/V the surface-to-volume ratio, Θ_D and q_D the Debye temperature and wave vector for the bulk.

Figure 6 shows the behavior of the σ^2 as evaluated using this new formula for gold clusters. The increase of the σ^2 values, with respect to the bulk value (due to the surface modes), is not negligible (Fig. 7) since it reaches a value of about 25% for the 15-Å clusters. This confirms our previous statement that it is not possible to evaluate the Debye temperature for clusters using the asymptotic formula given by Eq. (5). Also the correlation factor changes between the bulk and the clusters [5% for the 15-Å clusters (Fig. 8)].

On the other hand, Fig. 6 shows an excellent agreement between the theoretical behavior and the experimental data of Table II. It follows that the dynamical properties of gold clusters are well described by the free-bounded-sphere density of states in a Debye approximation, also in agreement with heat-capacity measurements. It gives also a strong support to the macroscopic sphere model which is able to fully explain the structural and dynamical properties of our gold clusters.

As for the Debye temperature, the agreement found between our formula for the clusters EXAFS σ^2 and the experimental values, means also that the behavior of the clusters Θ_D, is well described by the normalization condition, Eq. (7), in agreement with the theoretical predictions of Chouchman and Karasz.[15]

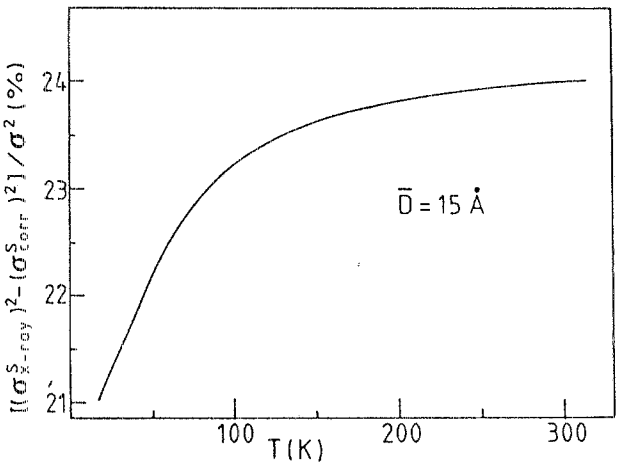

FIG. 7. Ratio between the surface contribution $[2(\sigma_{\text{x-ray}}^S)^2-2(\sigma_{\text{corr}}^S)^2]$ and the total σ^2 as a function of T for a 15-Å cluster.

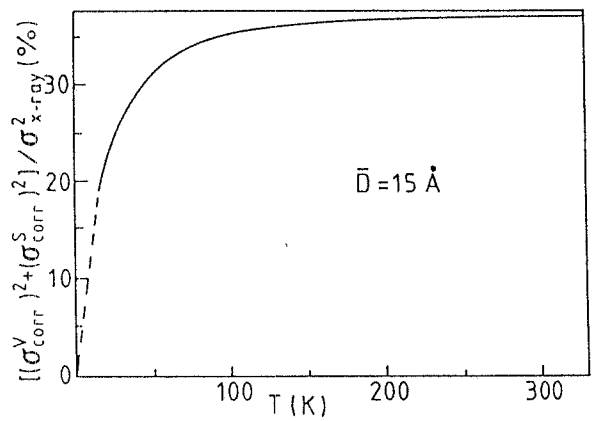

FIG. 8. Thermal behavior of the correlation factor $[2(\sigma_{\text{corr}}^V)^2+2(\sigma_{\text{corr}}^S)^2]/(2\sigma_{\text{x-ray}}^2)$ for a 15-Å cluster diameter.

Finally, it is interesting to note that in the clusters, the origin of the NN distance contractions and of the increased Debye-Waller factors is the same: the presence of a high surface-to-volume ratio. So, in all the cases where the surface is not so well defined, like in the hydrogen-reduced catalysts or where a strong metal-support interaction is present, the NN distance contractions and the σ^2 increase must be much lower. Until now, there have been several studies on catalysts which show the first of these two effects. In the future it will also be interesting to investigate the second one and the correlations between the two.

IV. CONCLUSIONS

In conclusion, we have shown that it is possible to determine the Debye temperature of gold metal from the behavior of the EXAFS σ^2 factors as a function of the temperature. We showed that it is not possible to describe the cluster phonon spectrum as that of the bulk in terms of a lowering of the Θ_D. Finally using a new theoretical formula for EXAFS σ^2 values which takes into account explicitly the surface mode contribution to the uncorrelated atomic root-mean-square displacement, we obtained an excellent agreement with experimental σ^2 values previously reported.

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