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CHARACTERIZATION OF SMALL METALLIC CLUSTERS
BY ELECTRON ENERGY LOSS SPECTROSCOPY

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Abstract

Small spherical tin and gallium clusters (diameters in the range 2 to 80 nm), prepared with a liquid metal ion source, were analysed in a scanning transmission electron microscope (STEM) by electron energy loss spectroscopy (EELS). Both volume and surface plasmon excitations were investigated and their dependence on the cluster size interpreted by classical and quantum mechanical models. A blue shift of the volume plasmon energy with decreasing radius R of the cluster was clearly detected. The full width at half maximum (FWHM) of the peak, related to the damping of the volume plasmon excitation, showed a dependence in $1/R$. The reported variation of the surface plasmon energy with R was consistent with earlier predictions or experiments.

Introduction

Electron Energy Loss Spectroscopy in the electron microscope is now considered by many microanalysts as a powerful technique for getting local information (chemical, electronic properties) on a wide variety of specimens. From a historical point of view, the low loss region ($0 \rightarrow 100$ eV) in an EELS spectrum was first investigated and the relevant peaks interpreted as a manifestation of collective excitations of the electrons lying in the conduction or valence bands of the solids. From the early beginning, El Hili [8] used these plasmon excitations as a method for chemical analysis in aluminium based alloys. Many authors [16,24] tried to correlate the energy value of the plasmon loss in an EELS spectrum with a local measurement of the chemical composition.

After the work of Wittry et al. [25], Colliex and Jouffrey [6] and Isaacson [11], most of the microanalysis studies using EELS were carried out with the high energy loss region (100 eV \rightarrow a few keV): the local character of the information seems to be more effective in that case, since the inelastic event is confined inside the shell of an atom.

But, during the last few years, the technology involved in modern instruments (dedicated STEMs or conventional TEMs -CTEMs- with scanning attachments) enables us to reconsider the problem of the localization of both core excitations and plasmon losses: probe sizes down to the sub-nanometer range and electron spectrometers corrected from second order aberrations are well suited for a close examination of the excitation processes [1,7]. The present work deals with the problem of collective excitations in small clusters, and tries to give an answer to a few "naive" questions:

. How can a volume plasmon be excited in a medium of very small dimensions?

. How do the free surfaces of the cluster act on the volume and surface plasmon intensities, energies and widths?

. When the energy of a volume plasmon is slightly shifted from its original position, can we only speak about this effect in terms of "chemical" shift? (in other words: is the

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variation of the plasmon energy loss a valid criterion of chemical or electronic composition modification ?).

In the following, we investigate experimentally the energy position and full width at half maximum (FWHM) of volume and surface plasmons excited in small gallium and tin spherical clusters. We compare both classical and quantum mechanical theoretical models. Localization problems are still under examination and the results will be published in the future.

Materials and Methods

Specimen preparation

Benefit is taken of our experience in the technology of the liquid metal ion sources (LMIS) for the preparation of the specimens. As shown in figure 1 an LMIS is made of a tank, filled

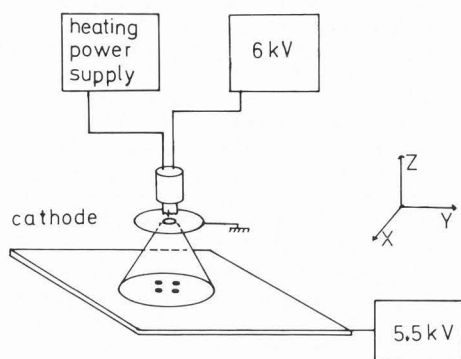


Fig. 1 - General scheme for the specimen preparation with a Liquid Metal Ion Source (LMIS).

with liquid metal, and a support (tungsten tip) at the apex of which an ionic emission is created. In front of the tip, and very close to it (a few millimeters), a high voltage (6 kV) cathode defines the intense electric field responsible for the emission. In the center of the cathode, a small hole allows the emission products to go through and reach the specimen support which is simply composed of a set of 4 standard grids (as used in electron microscopy), covered with a very thin (less than 10 nm) carbon layer. A decelerating voltage (5.5 kV) is applied on the grids in order to avoid any excessive energy transfer during the deposit of the metal on the carbon layer.

It has been shown [21] that the distance between the tip apex and the cathode is a very critical parameter governing, among others, the intensity of the emission: the liquid metal covering the apex builds a Taylor cone figure, and an emission of electrically charged droplets can be obtained, the size of which is proportional to the emission current. These droplets are collected by the grids and form a population of spherical clusters with diameters varying from 1 to a few hundred nanometers.

The experimental conditions are: vacuum better than 10^{-6} torr, emission current 70-100 microamps, exposure time 1 to 2 hours. This unconventional way of using LMIS revealed itself to be very efficient for the preparation of our metallic clusters. The only restriction is that the liquid metals used must have a good surface diffusion factor on the tungsten tip.

Preliminary characterization

All the specimens are checked before EELS analysis by selected area diffraction on a CTEM. Most of them are oxidized. Actually, EELS experiments hereafter described show that the oxidation is only superficial (1-1.5 nm for gallium and 2-3 nm for tin clusters). A few metallic gallium clusters are however obtained by quickly transferring the grids, under permanent argon flow, from the preparation chamber to the microscope.

X-ray microanalysis performed in the STEM reveals that the specimens are chemically pure.

Experimental equipment and setup

EELS experiments are carried out on a dedicated STEM (VG HB501) run at 100 keV and fitted with a second order aberration corrected electron spectrometer (GATAN 607) routinely capable of sub-1 eV energy resolution for a solid half angle of collection of ~ 5 mrad. A complete description of the whole system (microscope and microcomputers), together with its ultimate performances can be found in [7]. We want only to point out here that a very small probe (diameter ~ 0.7 nm) can be focused on a given cluster, and the relevant diffused electrons collected either by an annular dark field detector or a bright field detector located just behind the electron spectrometer.

The EELS spectra are digitally recorded using HAMLET software [23]. As already mentioned [22], we pay attention to acquisition conditions to avoid any non-linearity problems due to various artefacts as non-constant dead times of the counting electronics. A detailed description of the spectra acquisition and processing techniques can be found in [2]. Original EELS spectra before and after processing are also displayed in this reference.

Volume Plasmon Energy Function of the Cluster Size

Theoretical considerations

It is well known (see for example [18]) that plasma oscillations in infinite media can be related, in the electron gas model, to the condition: $\epsilon(\omega) = 0$, where $\epsilon(\omega)$ is the complex dielectric function of the solid. The solution of this equation is usually called:

$$\omega^2(q=0) = \omega_p^2 = \frac{4\pi n e^2}{m} \quad (\text{C.G.S.}) \quad (1)$$

and the dispersion relation, that is the variation of the plasmon frequency $\omega(q)$ with its wave vector q can be approximately written:

$$\omega^2(q) = \omega_p^2 + \frac{3}{5} v_F^2 q^2 + 0(q^4) \quad (2)$$

(v_F = Fermi velocity)

When the experiment is performed in a STEM, geometrical considerations on the finite aperture sizes must be taken into account. In our geometry, the half angles of illumination and collection are respectively 7.5 and 2.7 mrad. In a first approximation, neglecting plural scattering, the maximum angle of scattering of the collected electrons is therefore 10.2 mrad, which defines a maximum value of the transferred wave vector $q_{\max} = 17.3 \text{ nm}^{-1}$.

This value of q_{\max} is larger than the critical wave vector $q_c = \omega_p/v_F$ (typically $\sim 12 \text{ nm}^{-1}$). So, the dispersion relation given by formula (2) must be integrated from $q \sim 0$ to $q \sim q_c$; the behaviour of $\omega(q)$ for $q > q_c$ being still rather imprecise.

Two other effects are also included in the measurements discussed below :

a) in a cluster of radius R , the minimum value of q is π/R : the maximum wave length of the charge fluctuation inside the cluster has to be smaller or equal to the diameter, in order to keep the electrical neutrality of the cluster. The integration over q must therefore be done from π/R to q_c .

b) for large clusters, the total thickness $2R$ of the sample (we neglect the carbon layer thickness) can be large enough to allow multiple (mainly double) scattering. It is beyond the scope of this paper to give a detailed formulation, in terms of convolution products, of the different possibilities for mixing elastic and inelastic scattering events. Since the angular distribution of an elastic scattering is generally wider than the inelastic one, we merely consider here the elastic scattering to be responsible for a momentum transfer q_{el} large enough to prevent the collection of electrons having suffered an inelastic momentum transfer $q_{in} > q_{min}$. In other words, we suppose in this crude model that the angular distribution of the elastic cross section is peaked at $q_{el} = q_{\max} - q_{min}$. Obviously, we neglect all the multiple processes in which :

$$q_{in} > \frac{\pi}{R}$$

and the elastic momentum transfer either greater or smaller than q_{el} .

Weighting the different probabilities, the actual measured energy of the volume plasmon should be :

$$\hbar\omega = \frac{\hbar\omega(q_{\text{mean}}) + \frac{2R}{\lambda_e} \cdot \hbar\omega(q_{\text{min}})}{1 + 2R/\lambda_e} \quad (3)$$

with λ_e = mean free path for elastic scattering, and

$$\hbar\omega(q_{\text{mean}}) = \frac{\int_{\pi/R}^{q_c} \hbar\omega(q) \frac{2\pi}{q} dq}{\int_{\pi/R}^{q_c} \frac{2\pi}{q} dq} \quad (4)$$

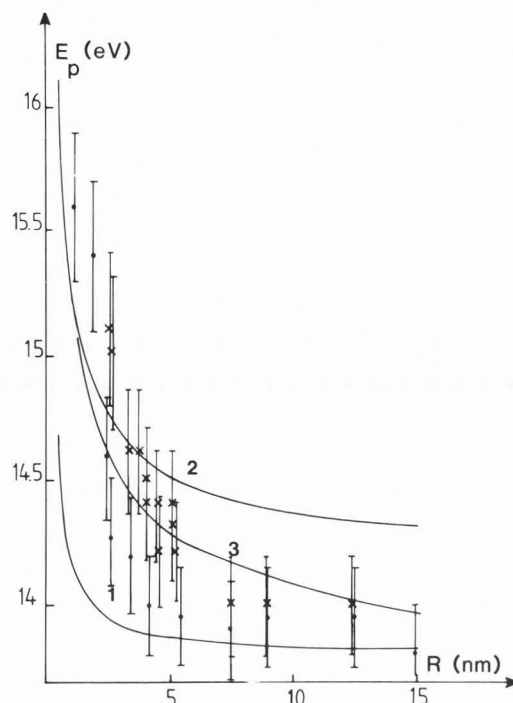


Fig. 2 - Variation of the volume plasmon energy in metallic (dots) and oxidized (crosses) gallium clusters. (1) : macroscopic effects of surface pressure, (2) : integration of the dispersion relation, (3) : same as (2) with double scattering processes included.

Experimental results

We have plotted on figures 2 and 3 the measured energies of the volume plasmon, versus the cluster radius, in metallic gallium, oxidized gallium and tin. A blue shift with decreasing R is clearly detected. The comparison of the two experimental curves (dots and crosses) in figure 2 reveals that the radii of oxidized gallium clusters are overestimated. These radii are measured on dark field images which include of course the oxide layer. By a close comparison of the two figures, this surface layer can be estimated, for the gallium case, to be in the range 1-1.5 nm.

On the same figures, we have plotted three "theoretical" curves :

- curves(1) are obtained by macroscopic considerations on the surface pressure applied on small aggregates. The general trend of this surface pressure, which increases with decreasing radius, is to reduce the volume in which are enclosed the conduction electrons, and therefore to raise the energy of the volume plasmon. These macroscopic effects are doubtless insufficient to explain the behaviour of our results.

- curves(2) show the result of a simple integration from q_{\min} to q_c of the dispersion relation (equations (2) and (4)). The agreement for the small clusters is rather good. A discrepancy

Surface Plasmon Energy Function of the Cluster Size

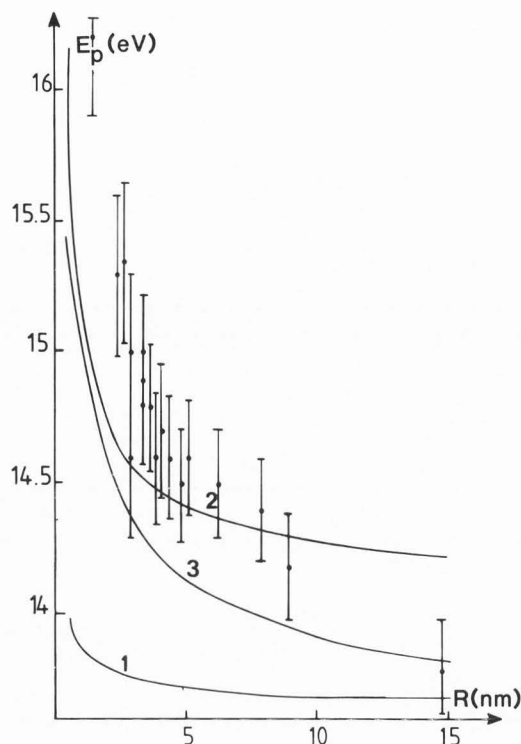


Fig. 3 - Variation of the volume plasmon energy in oxidized tin clusters. (1) : macroscopic effects of surface pressure, (2) : integration of the dispersion relation, (3) : same as (2) with double scattering processes included.

persists for large clusters.

- curves (3) are deduced from curves (2) and take into account the double scattering events as described by equation (3) : for the smaller radii, the correction is negligible, but for the larger ones, the higher probability of collecting electrons which are elastically scattered at large q slightly reduces the volume plasmon energy.

The agreement of these curves (3) with the experimental results confirms that this blue shift of the volume plasmon energy is mainly due to dispersion effects. It must be pointed out that clusters with radii larger than 5 nm can be considered, from a dispersion point of view, as infinite medium. The energy of the volume plasmon is constant (within the accuracy of the measurement), and 13.8 eV (for gallium) and 13.7 eV (for tin) are the values already reported [18] for thin films.

In the tin case, the curve (3) of the figure 3 should be translated by 2 or 3 nm for a satisfactory explanation of the results. Here again, it is a matter of oxide layer thickness.

Theoretical considerations

The problem of the surface plasmon creation can be solved by the hydrodynamical model proposed by Bloch [5]. In this model, it is assumed that all the physical quantities describing the complete system state (potential energy, external pressure, ...) can be expressed in terms of electronic density, and the collective electronic motions are thus a function of a departure from the equilibrium state of the electronic density.

This model has been successfully applied by Jensen [12], Natta [17] and Ruppin [19,20] in the case of small metallic spherical clusters. The potential created by the surface plasmon is projected on the spherical harmonics set $Y_{\ell,m}(\theta,\phi)$, and the resonance frequency satisfies the following condition :

$$\frac{2\ell + 1}{\ell} \cdot \left(\frac{\omega}{\omega_p}\right)^2 - 1 = \frac{\ell + 1}{qR} [J_{\ell}(qR)/J'_{\ell}(qR)] \quad (5)$$

with $J_{\ell}(qR)$ = spherical Bessel functions.

The "classical limit" is reached for $qR \gg 1$:

$$\frac{2\ell + 1}{\ell} \cdot \left(\frac{\omega}{\omega_p}\right)^2 = 1 \quad (6)$$

The case $\ell = 1$ (dipolar case) is the classical solution $\omega_p/\sqrt{3}$ for a small sphere, as predicted by the Mie^P theory, while the limit case $\ell \rightarrow \infty$ is related to the thin film case : $\omega_p/\sqrt{2}$. The value to be given to ℓ is, for intermediate cases, function of the local curvature, and Fujimoto and Komaki [9] gave the relation between these two parameters.

Ruppin's work [19,20] confirms that both surface and volume plasmons energies must increase with decreasing R , the refinements introduced to take into account a diffuse surface, i.e., the fact that the electronic density goes continuously $\rightarrow 0$ when $r \rightarrow R$, keeps the general tendency in $1/R$.

Experimental results

The results are displayed on figures 4 (gallium) and 5 (tin). A general trend can be extracted from these data.

For gallium, the limit values $\hbar\omega_p/\sqrt{3} = 7.97$ eV and $\hbar\omega_p/\sqrt{2} = 9.76$ eV are obtained, and for intermediate values of R , we can define a mean value $\langle \ell \rangle$ which increases from 1 to infinity with increasing R .

For tin, the presence of a more important oxide layer induces a modification of equation (6) which must be written as follows :

$$\frac{\ell + (\ell+1) \epsilon}{\ell} \cdot \left(\frac{\omega}{\omega_p}\right)^2 = 1 \quad (7)$$

with ϵ = dielectric constant of the oxide. The comparison of the limit values $\ell = 1$ and $\ell \rightarrow \infty$, given by this equation, with our results suggests that one uses the value $\epsilon = 1.5$. This rather low value for ϵ can be due to the small oxide thickness. Using this value for ϵ and

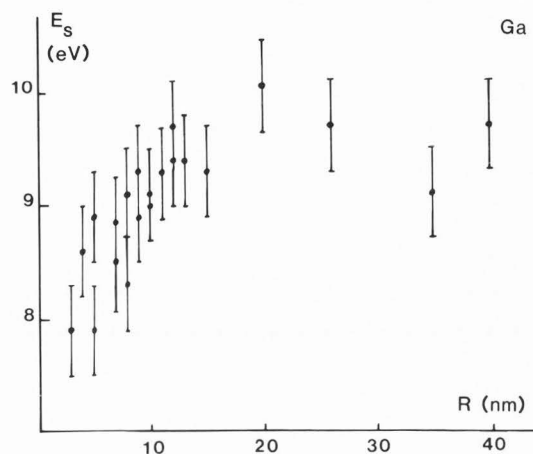


Fig. 4 - Variation of the surface plasmon energy in metallic gallium clusters.

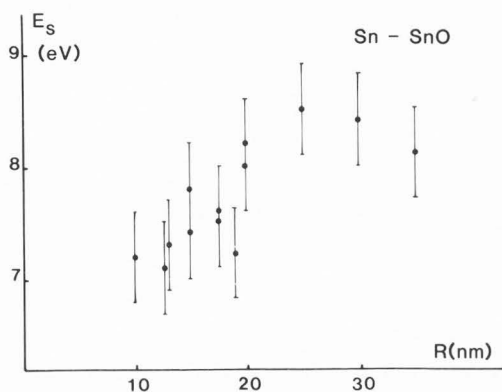


Fig. 5 - Variation of the surface plasmon energy in oxidized tin clusters.

$\hbar\omega_p = 13.7$ eV, the two limits should be 6.9 eV ($\ell = 1$) and 8.7 eV ($\ell \rightarrow \infty$) and have to be compared to the experimental ones : 7.15 eV and 8.4 eV.

Another approach can be followed for checking the surface plasmon energy of metallic clusters (radius R_0) covered by an oxide layer (total radius R_1) : in his study on small aluminium spheres, Batson [4] stated a formula giving the surface plasmon frequency as a function of $\gamma = R_1/R_0$ and ϵ , the frequency dependent dielectric constant :

$$\left(\frac{\omega_p}{\omega}\right)^2 - 1 = \epsilon \left(\frac{\ell+1}{\ell}\right) \cdot \frac{\gamma^{2\ell+1}(\epsilon\ell+\ell+1) - \ell(\epsilon-1)}{\gamma^{2\ell+1}(\epsilon\ell+\ell+1) + (\ell+1)(\epsilon-1)} \quad (8)$$

In the limit $\gamma \rightarrow 1$, equation (8) is similar to equation (6) : for large clusters ($R_1 \sim 30$ nm), the oxide layer is negligible and the limit $\hbar\omega_p/\sqrt{2}$ is reached for large ℓ values.

For small clusters ($R_1 = 10$ nm, $\ell = 1$), equation (8) enables us to check the consistency between the oxide thickness ($R_1 - R_0$) and the dielectric constant at the surface plasmon frequency. If we assume the above value 1.5 for ϵ , solving equation (8) with $\hbar\omega_p = 13.7$ eV, $\hbar\omega = 7.15$ eV gives $\gamma \sim 1.5$, that is $R_1 - R_0 = 3.3$ nm. This is consistent with the observations made during the preliminary characterizations.

Damping of the Volume Plasmon

Theoretical considerations

It is well known [18] that in solids, the damping of volume plasmons is mainly related to vertical ($q = 0$) and non-vertical ($q \neq 0$) interband transitions. Following Hasegawa's ideas [10], it is possible to describe the FWHM of the volume plasmon peak ($\Delta E_{1/2}(q)$) with a dispersion relation :

$$\Delta E_{1/2}(q) = A + B q^2 + O(q^4) \quad (9)$$

It must be pointed out, however, that :

- some linear dependence at small q values can be found in experimental reports.
- the coefficient B in the above formula is only approximately known. Even its sign can vary, depending upon which process for damping is under examination : interband transitions, electron - electron or electron - phonon interactions.

In clusters, the presence of a surface limiting the medium acts also as a damping factor. From a classical point of view [13], it reduces the mean free path of the electrons collectively excited by the plasmon, and it can be shown that, in spherical clusters, the imaginary part ϵ_2 of the dielectric function is dependent on the cluster radius R according to the formula :

$$\epsilon_2(\omega, R) \sim \epsilon_2(\text{bulk}) + \frac{\omega_p^2}{\omega^3} \frac{V_F}{R} \quad (10)$$

Note that the FWHM of the plasmon peak $\Delta E_{1/2}$ is related to ϵ_2 as :

$$\Delta E_{1/2} = \hbar\omega_p \cdot \epsilon_2 \quad (11)$$

Quantum mechanical effects [14,15] are quite different : the surface does not act as a reflecting wall for the excited electrons, but simply quantifies the different energy levels that an electron, enclosed into a box, can reach. The energy width of these levels is a function of the temperature, but if the energy separation of these levels (proportional to $E_F/N^{2/3}$) is larger than its width, electronic transitions are then possible which reduce the life time of the plasmon. A complete calculation of this effect [19] shows that in this approach, the FWHM of the plasmon peak has, like in the classical model, a dependence in $1/R$; the quantitative factor being, however, 2 or 3 times smaller than the classical one.

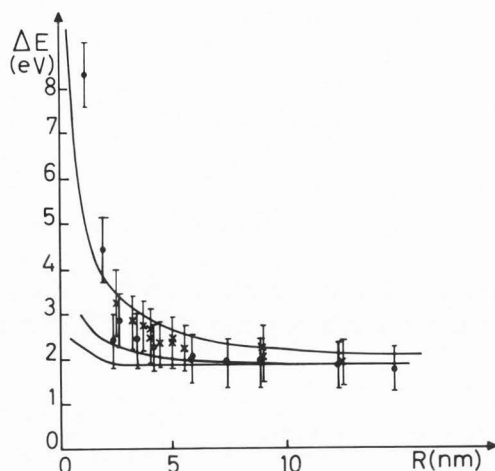


Fig. 6 - The curves of figure 7 are vertically translated to take into account the bulk component of the volume plasmon damping. Comparison with experimental results on metallic (dots) and oxidized (crosses) gallium clusters.

Experimental results

We reported on figure 6 our measurements of the FWHM of the volume plasmon peak for metallic and oxidized gallium clusters ($R : 2 \rightarrow 15$ nm). As already noticed, the asymptotical behaviour is reached for $R > 5-7$ nm. Such big clusters present a FWHM which is mainly independent of the presence of the surface and can be written as :

$$\Delta E_{1/2} = \hbar \omega_p \cdot \epsilon_2(\text{bulk}) \quad (12)$$

The theoretical predictions are plotted on figure 7. Even the classical model is not sufficient to account for the experimental results. Actually, for the same reasons as those already discussed about the plasmon energy, we have to integrate the dispersion law (equation (9)) from q_{\min} up to q_c . Since no theoretical values of B is available (to our knowledge), we can only estimate, by an empirical fit, which value of B to take, in order to match our experimental results. For gallium, we found $B = 0.08$ eV.nm² and $\hbar \omega_p \cdot \epsilon_2(\text{bulk}) = 0.7$ eV. (For tin, the corresponding values are $B : 0.16$ eV.nm² and $\hbar \omega_p \cdot \epsilon_2(\text{bulk}) = 0.5$ eV). These results are plotted (curve 3). The curves displayed on figure 6 are just the same, but vertically translated in order to take into account the bulk component of the damping. Although the agreement is not perfect, it seems obvious that the dispersion relation is an important factor for a complete understanding of such experiments.

Earlier work done by Batson [3] on small aluminium spheres already noticed the $1/R$ dependence of the FWHM of the volume plasmon. Moreover, this author pointed out that the angular dependence of plasmon scattering needed to be investigated to determine the importance of damping due to the plasmon wave length.

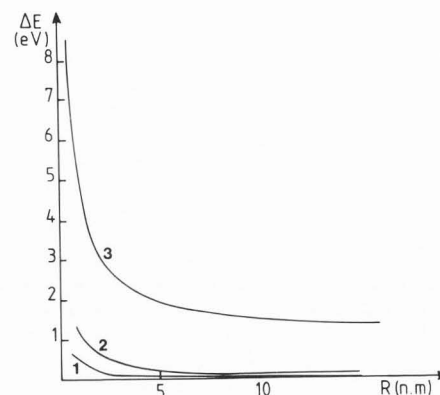


Fig. 7 - Theoretical predictions of the volume plasmon FWHM in gallium due to cluster size effects. (1) : Quantum model (2) : Classical model, (3) : Classical model with integration of a dispersion relation.

Conclusions

This study of the collective excitations in small metallic clusters raises important conclusions on a twofold point of view :

Concerning the fundamental aspects of the physics involved in these experiments, the dispersion relations of the volume plasmon energy and damping have to be integrated from q_{\min} to q_c , q_{\min} being dependent on the cluster size, in order to be compared with the results obtained with a STEM. We think that the surface plasmon behaviour is accurately described by the hydrodynamical model. Energy positions can be predicted.

Concerning the implications in chemical analysis at the nanometer scale (nanoanalysis), it is clear that erroneous results can be obtained in special geometries if any energy shift of the plasmons is systematically correlated to a modification of the chemical composition. More attention must therefore be paid to the analysis of specimens containing microcrystals or very small grains.

The use of surface plasmon excitations should be, in the coming years, a very powerful tool for surface imaging with a sub-nanometer spatial resolution.

Acknowledgements

We are grateful to our colleagues J. Van de Walle for kindly preparing the specimens and A. Nourtier and C. Noguera for guiding us in the various theoretical models and calculations. Dr. H. Kohl, from Darmstadt (W.Germany) helped one of us (M.A.), by special calculations, discussion and comments during the preparation of the thesis presented in Orsay on this subject [1].

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Discussion with Reviewers

O.L. Krivanek : What was the precise thickness of the carbon substrate ? If it was close to 10 nm, it seems that the theory should try to take explicit account of excitations involving both the particle and the substrate, since the smallest particles studied are only 2 nm in diameter. Is there any simple way to model such interaction ?

Authors : We did not make any precise measurement of the thickness of the carbon substrate. The value of 10 nm is stated from the intensities ratio between the carbon volume plasmon and the zero-loss peak in EELS spectra recorded on areas without clusters. Obviously, the presence of carbon disturbs our analysis on both surface and volume plasmons [1,2]. We did not find a simple way to model the interaction between the particle and the substrate.

O.L. Krivanek : The melting temperature of Sn and especially Ga are so low as to make melting the cluster due to the energy deposited by the electron beam almost inevitable. In a line scan, the phase transformation would presumably happen as the probe partially enters the cluster. (There is also the interesting complication of having a liquid metal cluster covered by a solid oxide layer). Could the authors comment on the effect of the phase transformation on the plasmon energy ?

Authors : Our specimens have been observed with a high resolution electron microscope JEOL 200 CX.

Dark field images obtained at high magnification for two perpendicular directions of elastic scattering show uncorrelated speckle patterns [1]. Therefore, there probably exists no local inhomogeneous order and we think that the clusters are completely amorphous, even liquid, into the solid oxide layer. We do not notice any phase transformation during the experiments.

A. Howie : Equation (5) can be rewritten more compactly and usefully as :

$$1 - \frac{\omega_p^2}{\omega^2} = \frac{\ell + 1}{\ell} \cdot \frac{J_{\ell+1}(qR)}{J_{\ell-1}(qR)}$$

This then covers both the bulk modes (q real) and the surfaces modes (q imaginary). For the bulk modes we then see (for $\ell = 1$), $J_2(qR) = 0$ i.e. $q_{\min} = 4.5/R$ rather than π/R as the authors assume. This may improve the fit between theory and experiment.

Authors : We agree with this reformulation of equation (5). The pole of $J_2(qR)$ gives however $q_{\min} = 5.76/R$ instead of π/R (or $4.5/R$). The fit between theory and experiment is worse : the dispersion relation increases the value of $\hbar\omega(q_{\text{mean}})$ when q_{\min} increases. For Ga, $R = 5$ nm, $\hbar\omega(q_{\text{mean}}) = 14.7$ eV (for $q_{\min} = 5.76/R$) instead of 14.51 eV (for $q_{\min} = \pi/R$). Therefore other effects must be included to account for the measurements, and we think that multiple scattering is one of them.

A. Howie : Has anyone observed bulk plasmon energy shifts in thin films due to the effects described by equation (3) ?

Authors : We are not aware of such experiments. Note however that equation (3) introduces no new effect : it merely balances, in a crude description, the single inelastic process and the mixed elastic-inelastic one.