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Phase transitions in gallium nanodroplets detected by dielectric spectroscopy

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Abstract. Both theoretical and experimental works give evidence that gallium exhibits solid phases labelled β, γ, δ, ϵ besides the stable α phase strongly dependent both on the size and the confinement conditions. An experimental technique was used based on capacitance and conductance measurements *vs.* temperature in the audiofrequency range. This technique is particularly sensitive to the conditions of the investigated particle surface that plays a fundamental role in the melting and more generally in the phase transition processes. In particular the strict relation between the derivative of the capacitance with respect to the temperature, $\mathrm{d}C/\mathrm{d}T$, and the entropy of the system is considered. In gallium nanoparticles 20 nm in radius, only the δ phase is shown to occur. Further the transition to liquid phase was detected. The melting process was found to start about 65 K below the full melting temperature value. In the case of particles 10 nm in radius, where different metastable phases may occur, the capacitance *vs.* temperature curve was found to display abrupt changes of the slope. The singularities are associated to a well defined transition temperature.

PACS. 65.80.+n Thermal properties of small particles, nanocrystals, nanotubes – 64.70.Nd Structural transitions in nanoscale materials – 77.22.Ej Polarization and depolarization – 67.57.Np Behavior near interfaces

1 Introduction

In this work we report capacitance measurements on metal (specifically Ga) nanosystems which are proved to bring new and detailed information on the size dependent premelting and melting process in an easily accessible temperature range.

The gallium presents, at the solid state for temperature lower than 302.8 K, a metallic molecular crystalline structure, named alfa-phase, stable in bulk with a covalent nature. Several investigations [1–4] proved the existence in small particles (below micrometric size) of different metastable structural phases named β, γ, δ, and ϵ. These phases have different transition temperatures lower than that of α: 237.4 K (γ), 244.4 K (ϵ), 253.6 K (δ) and 256.7 K (β). The metastable phases are depending on the growth procedure, size and confinement conditions of the Ga particles.

In the metallic nanometric clusters the phenomena related to the onset of order-disorder transition are precursor of the complex melting process (and associated premelting), may assume a particular relevance. In fact in the nanometric particles, the percentage of the atomic surface atoms, that are strongly involved in the premelting manifestations, is high with respect to the bulk [5–11].

In this paper an investigation is reported both on the onset of metastable crystalline phases in Ga nanoparticles (10 nm in radius) and on the manifestation of premelting (20 nm in radius).

The adopted dielectric spectroscopy technique represents a particularly sensitive probe to detect and study both the phase transition phenomenon and the melting precursor manifestation of melting for its peculiar characteristics: (i) specific dependence of the capacitance (directly connected to surface polarization) on the surface first atomic layers; (ii) close connection between capacitance and entropy of the explored system; (iii) high sensitivity to detect and study the phase transition evolution.

Measurements of transmission electron microscopy (TEM) were also accomplished with the aim of performing sample analysis and determining the whole particle melting temperature.

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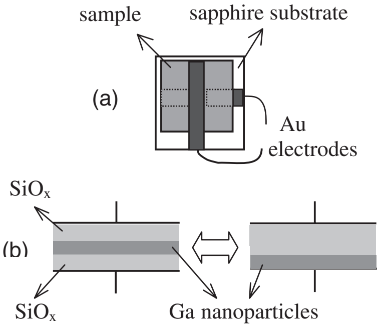

Fig. 1. (a) Cross arrangement of the Au electrode plain view; (b) two equivalent connections of the capacitors (matrix and Ga layers) in series.

Furthermore conductance measurements, simultaneously performed, are reported in order to have additional information for the analysis of the phenomena. It is important to note at this stage that in particular the capacitance data are connected to the onset of disorder strictly related to the surface of the nanoparticles and eventually amenable to the surface preroughening phenomenon as treated *e.g.* in reference [5]. This takes place before the manifestations of premelting and melting as detected by means of TEM.

2 Experimental details

The investigated samples were grown by an evaporation-condensation self-organized process in ultra high vacuum, by an alternate deposition of amorphous SiO$_x$ and Ga nanoparticles layers on a previous SiO$_x$ layer. The distribution is quenched and protected by an additional SiO$_x$ layer. The amorphous substrate does not induce any preferential orientation and avoids all restrictions related to lattice mismatch. The deposit doesn't wet (or just partially wets) the substrate, so that the formation of islands is favoured (Volmer-Weber mode). It is possible in this way to obtain a rather regular shape of the particles (truncated spheres) with a relative low size dispersion (<20%) [12]. The sample total thickness is 200 nm, 30 nm due to the Ga particles layer and 170 nm to the embedding matrix.

For the dielectric measurements, gold electrodes were deposited on the two opposite sides of the film with a cross-connected geometry that allows the evaluation of the area of application of the electric field (Fig. 1a). The value, obtained by means of a measurements with a microscope, was 1.215 mm^2. The system capacitance C_t is given by the relation $1/C_t = 1/C_m + 1/C$, where C_m and C indicate the capacitance due to matrix and the Ga clusters layer respectively (Fig. 1b). A sample without Ga nanoparticles has been grown as reference sample for the intrinsic matrix dielectric properties determination. Two different samples were grown with different particle size: 20 and 10 nm in radius (named here as Ga20 and Ga10 respectively).

In order to determine the crystalline solid phases and melting temperature, a transmission electron microscope (Philips CM30, equipped by EDS and EELS spectrometers with CCD camera) was employed.

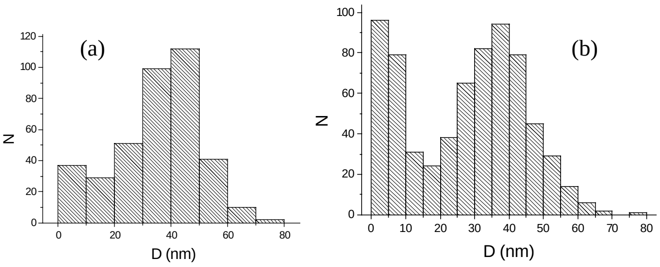

Fig. 2. Ga10 (a) and Ga20 (b) sample size distributions obtained by TEM.

The capacitance-conductance measurements were carried out, at 1 kHz, by a vectorial capacitance bridge (General Radio 1616A). To vary the temperature, a closed two stages helium cryostat was employed on the temperature range 30−300 K with a scan rate of about 1 K/min. A calibrated silicon diode was used for temperature monitoring.

3 Results and discussion

3.1 TEM

Preliminary TEM investigations were performed on both the Ga20 and Ga10 samples in order to control the shape and the size distribution of the metallic nanoclusters. The size distribution was confirmed to be lower than 20% (Fig. 2).

By increasing the temperature, TEM investigation as a function of temperature on Ga20 sample evidenced a solid-liquid transition of the Ga particles at the temperature $T_c = 250$ K. Hints of melting were identified about 5 K before T_c. The crystalline phase in the solid state was clearly identified as delta-phase with trigonal structure and cell parameters: $a = 9.087$ Å, $b = 9.087$ Å, $c = 17.022$ Å. These found values fully agree with the data reported in literature [4].

For the Ga10 sample, the whole melting was found to occur at the temperature about $T_c = 235$ K and the beginning of the process was observed at 230 K.

3.2 Ga20 sample

The Ga20 sample capacitance $C(T)$ as a function of temperature, starting from low temperatures, displays a positive slope evolving continuously to a maximum at $T = 185$ K after that the slope became negative as shown in Figure 3.

If a material of dielectric constant ϵ is subjected to an electric field E, the entropy of the system is $S = S_0(T) + (E^2/2)\mathrm{d}\epsilon/\mathrm{d}T$ that may be expressed as $S = S_0(T) + k(E^2/2)\mathrm{d}C/\mathrm{d}T$, $S_0(T)$ being the entropy in absence of the field and k a geometric factor. Therefore the entropy is increased by the field when $\mathrm{d}C/\mathrm{d}T$ is positive and is decreased when this quantity is negative. Since the

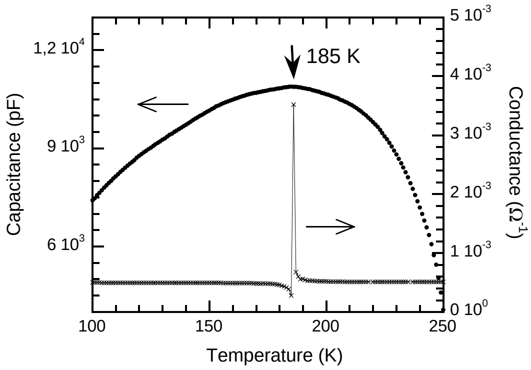

Fig. 3. Ga20 sample: capacitance (●) and conductance (×) of the gallium nanoparticles layer as a function of temperature in the range below the full melting temperature.

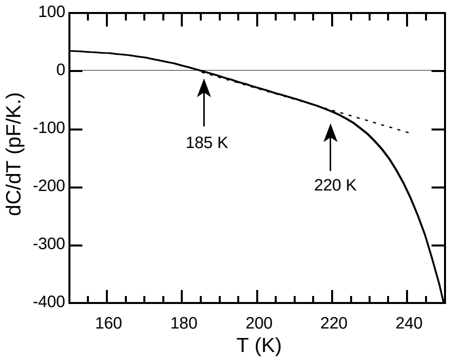

Fig. 4. Ga20 sample: the derivative of the Ga layer capacitance C as a function of T, *versus* temperature (solid line). The derivative is proportional to the entropy due to the applied field. The change of sign, at $T = 185$ K, evidences an order-disorder transition. The dotted line shows a linear behaviour in the 185−220 K interval.

entropy is a measure of the molecular disorder, the positive slope of $C(T)$ means that the applied external field reduces the degree of order while the negative slope indicates that the field produces order [13,14]. Therefore on the basis of merely thermodynamical considerations the transition from a positive to negative value for $\mathrm{d}C/\mathrm{d}T$, corresponds to a transition from an ordered phase to a disordered one. In fact while a positive slope of the capacitance is typical of the solid materials, the negative one is found only in liquid-like systems.

The obtained capacitance measurements prove that in Ga20, at the temperature $T = 185$ K, premelting phenomena are manifested. The atomic surface layers disorder shows up 65 K below the full core melting as detected by the TEM results.

The plot of the quantity $\mathrm{d}C/\mathrm{d}T$ (that is directly connected to the entropy) as a function of T (Fig. 4) clearly means that the degree of disorder increases with temperature to $T = 250$ K value.

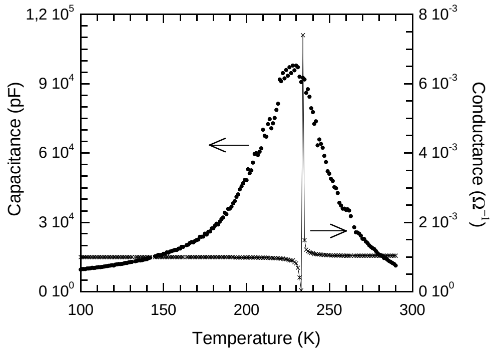

Fig. 5. Capacitance (●) and conductance (×) of Ga10 sample as a function of temperature.

3.3 Ga10 sample

In the Ga10 sample, the temperature dependence of the capacitance shows a relevant and structured peak. Correspondingly the conductance behavior *vs.* temperature exhibits a well defined and sharp peak with maximum at $T = 235$ K (Fig. 5).

In dielectric spectroscopy the presence of a peak, both in capacitance and conductance, is a typical manifestation of a phase transition occurring at the critical temperature value T_c of the maximum. In our case, the capacitance fluctuations at the top of the peak don't allow the precise determination of the maximum; on the contrary the corresponding conductance, due to its typically sharp lineshape, clearly indicates the peak position at $T = 235$ K that was therefore adopted as critical value T_c of the transition. The T_c value, determined from the dielectric response, agrees with TEM results that indicate a melting transition near $T = 235$ K. A closer inspection of the capacitance data evidences: (i) the top of the peak characterised by fluctuations without a well defined maximum; (ii) jumps and discontinuities in the plot line in the temperature range between 210 and 260 K, whose nature needs a deeper examination.

With the aim of obtaining more detailed information the capacitance C *vs.* the reduced temperature $T^* = |T - T_c|/T_c$ was considered and the plot was analysed in the frame of the general theory that predicts, for critical phenomena, the dependence of the considered property (C in our case) on T^* as a power-law both for $T > T_c$ and $T < T_c$. In this case, in the logarithmic scale, the plot appears as a straight line [15,16]. We point out that this analysis is along the lines for instance of reference [6] and that for nanoparticles below a given size melting is no longer considered a first order phase transition.

For $T < T_c$ (Fig. 6 inset) the plot of C *vs.* T^* shows a linear behaviour starting from low temperatures: $T^* = 0.57$ to $T^* = 0.148$ (from 100 to 210 K in terms of temperature) thus indicating that a phase transition is taking place and that $T_c = 235$ K, as given by conductance measurement, is working correctly. From the T^* value corresponding to $T = 220$ K, a flat line is displayed. The fact that the capacitance does not depend on the reduced

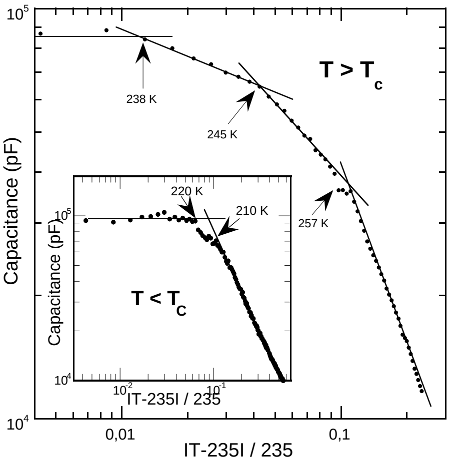

Fig. 6. Capacitance of Ga10 sample *vs.* reduce temperature $T^* = |T - 235|/235$ for $T > T_c$. Inset: capacitance *vs.* T^* for $T < T_c$ of the same sample. The same T_c value 235 K, was employed both for $T < T_c$ and $T > T_c$ regions.

temperature T^* (flat part) is indicative of the coexistence of different phases.

For $T > T_c$ the C *vs.* T^* plot displays a set of linear segments abruptly changing slope for T^* values that correspond to $T = 257$, 245, 238 K (Fig. 6). It is significant that such values agree with the critical values reported in literature for β, ϵ, γ crystalline phases transitions.

In conclusion the Ga10 capacitance and conductance data show, in agreement with the TEM results, that the Ga nanoparticles undergo an order-disorder transition at the temperature of about 235 K. In particular the power-law analysis of the capacitance data shows one solid phase at low temperatures until about 220 K and a coexistence of different phases up to 238 K. Increasing the temperature, the $C(T^*)$ plot gives an indication of a sequence of transitions through the metastable γ, ϵ, β phases identifiable by their critical temperatures reported in the literature. In this picture the cluster size, centred on the value of 10 nm in radius, appears to be, for gallium, a critical value to form the indicated phases for the confinement conditions present in the explored sample.

4 Conclusions

In this work we illustrate the very promising potentialities of a new approach to study the thermodynamic behaviour of metallic nanosystems, and in particular premelting and melting processes. The basis for this is given by the relationship between the derivate of capacity with respect to the temperature and entropy.

Initial surface disorder and progressive manifestation of melting can be detected and studied with a very high sensitivity, as shown also through the comparison with TEM data.

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