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Nanowires with well defined radii formed in operating liquid metal ion sources (LMIS)

P. Joyes, J. van de Walle, and R.-J. Tarento[a]

Laboratoire de Physique des Solides, bâtiment 510, Université d'Orsay, 91405 Orsay Cedex, France

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Abstract. For some elements such as germanium or tin, the mass spectra of ions emitted by liquid metal ion sources (LMIS) exhibit periodicities, i.e. series of equidistant peaks with an increase, ν, in the number of atoms between two peaks. We attribute it to the existence of jets in operating LMIS, the upper part of them being cylinders with $\nu-atom$ sections. The Ge_{6m+1}^{3+} and Sn_{6m+1}^{3+}, $m = 3$ to 8, and Ge_{6m+4}^{3+}, $m = 9$ to 14, observed ions can be explained by this mechanism, here $\nu = 6$. We extend this mechanism to bismuth and gold and, in this last case, it allows the interpretation of a yet unexplained Au_8^{3+} ion.

PACS. 36.40.-c Atomic and molecular clusters – 79.70.+q Field emission, ionization, evaporation, and desorption

1 Introduction

After the discovery of carbon nanotubes [1] many other elements or compounds were found to develop the same kind of structures: gold [2,3], platinum [4], silicon [5]. The modes of formation of these nanowires are diverse. Among them, one may mention the use of a STM (scanning tunneling microscopy) geometry. In this method the STM tip is dipped into the substrate and then withdrawn. The matter is stretched by the tip and thin suspended nanowires can be observed.

One may guess that such linear structures could also be produced by applying a strong electric field to a viscous medium or a liquid metal. The field would take the role of stretching or attracting the matter played by the tip in the overmentionned touch-and-away process. Of course, as the nanowires are no longer suspended they certainly will be unstable and, consequently, hardly observable. Nevertheless, we will show in this paper that their existence is indirectly revealed by analyzing the polyatomic species emitted by a LMIS (liquid metal ion source). For some elements, the mass spectra exhibits, among other features,remarkable series of peaks distant from each others by a constant number, ν, of atoms. In this paper, we attribute this periodicity to the emission mode: we show that likely these peaks are emitted from cylindrical jets with ν atoms in their section.

We first give, in Section 2, several arguments which lead to thinking that nanowires may appear in LMIS. In Section 3, we shortly describe the various LMIS emission modes and try to predict what could be the characteristics of the emission from nanowires. In Section 4, we compare these previsions with known experimental data on germanium, tin and bismuth. The case of gold is studied in Section 5 where we give a new detailed LMIS mass spectrum.

2 Nanowires in LMIS

The existence of nanowires in LMIS is likely. Various arguments can be brought to justify this point.

2.1 High voltage electron microscope observation

High voltage transmission electron microscope (HVTEM) observation made by Benassayag, Sudraud and Jouffrey [6] on an operating Ge LMIS shows that extremely thin jets are produced. Diameters of the order of 3 nm were observed. Theoretical models developed by Swanson and Kingham [7] also lead to this order of magnitude. More recently Forbes [8] shows that the main physical points are contained in a relatively simple 3-equation system. The equations express respectively firstly the Bernoulli law, secondly the balance between surface tension and electrostatic pressure at the top of the jet where a hemispherical shape is assumed and thirdly the electrodynamical expression of the total emitted current I. The known parameters are the current I (measured) the extraction field $F \sim 15$ V/nm for gallium and the surface tension $\gamma = 0.72$ N/m for gallium. The quantities to be calculated are the diameter, the ion velocity and the pressure at the top of the jet. By doing so, Forbes obtains a 3 nm diameter consistent with experimental data.

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[a] e-mail: `tarento@lps.u-psud.fr`

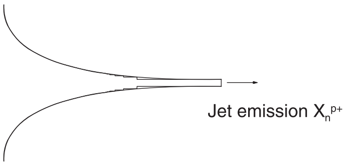

Fig. 1. Schematic representation of a jet shrinking by steps down to the atomic size of the thinnest nanowire.

Then, we see that the jet structures do exist in LMIS which are only five times the diameter of a typical one-shell nanowires (a 6-atom hexagonal section with 0.3 nm bonds has a 0.6 nm diameter).

2.2 Stabilisation of thin shapes by electric fields

As we already see the electric field is very large at the apex of a LMIS tip. The extraction field F, i.e. the smallest field needed to extract an atomic X^+ ion from a X sample, can be derived from low-temperature field evaporation experiments [8]. For a large number of elements there is a general agreement between the experimental and theoretical values [9] though some anomalies appears for Al and Au [8]. We notice that the F values are of the order of several tenths of V/nm (from 10 to 50 V/nm), depending on the elements.

Simple electrostatics shows that surface electric field increases with surface charge density and local curvature. A consequence of this appears if we consider finite conducting media where elongated shapes are stabilized when they are submitted to an electric filed. Physically the phenomenon is simply due to the repulsive forces between surface charges which decrease in elongated objects. The previous physical behaviour can be extended to jets appearing at the surface of a liquid phase. In this last case, the electrostatic problem cannot be so easily modelized as in a simple finite shapes but, physically, the same conclusion is expected: the jet will elongate and its radius will decrease in order to minimize the electrostatic repulsion. If the jet diameter were to decrease as expected from the preceding argument, from the observed 3 nm down to the atomic discretization should appear,leading to a shape schematised in Figure 1.

3 Various emission modes

The ion emission from a LMIS has been widely studied by mass spectrometry [10–13]. The energy [14] and angular [15] distributions of the emitted species have also been measured.

The largest part of the monoatomic and polyatomic emitted species is monocharged (X_n^+). These ions are emitted in two ways: either directly extracted from the surface by the usual field emission mechanism or produced by the explosion of metastable large droplets at some distance of the tip. These two possible (X_n^+) are revealed by their energy distribution where two peaks are observed [13,14], the particles emitted by the explosion of droplets being retarded in respect to those emitted from the surface.

The very thin cylindrical jets discussed before, even if they are unstable, will also be a possible source of emission. At the top of these structures the curvature is larger than in the other emitting region of the tip and, consequently, the charge density and the electric field are much stronger. Then we expect that the emitted ions will take a large p^+ charge ($p > 1$). Moreover, the matter being stretched along the field direction, the interatomic spacing becomes large and the bonding is lowered along the cylindrical axis. Then the electric field will easily extract slices of matter like in a cleavage. Suppose now that the highest part of the tip (see Fig. 1) has a section of ν atoms, then we can expect the emission of $X_{m\nu}^{p+}$ ions with $p > 1$, m being a variable integer giving the width of the slice.

4 Jet emission in germanium, tin and bismuth

The LMIS mass spectra obtained for tin [11] and germanium [12] show a remarkable modulo$-$6 periodicity with peaks for X_{6m+1}^{3+}, $m = 3$ to 8. This result agrees with the previous hypothesis and would reveal in operating LMIS the presence of jets with a $\nu = 6$ atom section. In the case of germanium, a second series of Ge_{6m+4}^{3+}, $m = 9$ to 14 is also observed [12]. We notice that additional atoms (1 in the first series; 4 in the second) are present in the emitted aggregates. They are certainty due to the presence of a cap of atoms at the top of the jet.

Let us briefly discuss the observed $p = 3$ charge value. As expected p is larger than one, however one may wonder why only triply charged species are observed. One knows that the charge is limited by the Rayleigh limit. A $p = 3$ value is close to this limit and certainly beyond it for the smallest sizes ($n \lesssim 30-40$). Consequently, most of the triply charged aggregates present in the mass spectra are certainly unstable, nevertheless they are observed because their lifetime are larger than the time of flight, t_f, in the apparatus. For aggregate with $p > 3$ this condition between the lifetimes and t_f would no longer be fulfilled.

The energy distribution of the triply charged species has been measured. The Sn_{6n+1}^{3+} and Ge_{6n+1}^{3+} [16] curves present only one peak beginning at the energy origin. This is coherent with the proposed emission mode. Indeed, though this jet emission can occur far from the emission zone of X_n^+ ions produced by a direct field extraction (see Sect. 3), they leave the liquid at the same electric potential and, during their flight to the collector they receive the same total acceleration (per charge).

The LMIS mass spectrum of bismuth [13] also exhibits a periodicity for highly charged species with peaks for Bi_{8m+3}^{3+}, $m = 2$ to 5. Here our hypothesis leads us to thinking that jets with a 8$-$atom section are present in operating LMIS.

It is worth-noticing that $\nu = 6$ period and the existence of cylindrical group IV molecular species is confirmed by a work on Si_n^+ ions. Their reactivity with NH_3 is experimentally studied [16] and a series of maxima is obtained for 17-18, 23, 30, 36, 43-44 and minima for 14, 20, 25, 33, 39. We see that it appears a modulo-6 periodicity. Phillips suggested [17] that these clusters have cylindrical shapes: the

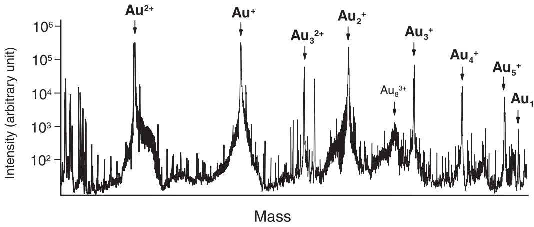

Fig. 2. Gold LMIS mass spectrum. The X_n^+ odd-even alternations mentionned in the text appear for $n > 5$, see also [20,21].

aggregates would be the stacking of six-membered rings. A calculation by Jelski et al. [18] shows that, indeed, Si_{36}^+ has a positive concentrated at each end and thus can easily react with NH_3 which is nucleophile. For Si_{39}^+ the situation is reverse with negatively charged ends.

Let us notice that in the forementionned works the 6-atom rings are supposed to be superimposed but other likely cylindrical structures can be explored.

5 Case of gold

We come now to gold. In this case, conductance measurements of thin nanowires have been made simultaneously with high resolution transmission electron microscopy observations (HRTEM) and "magic radii" were obtained. For example the smallest 2-shell gold nanowire has a central $n_1 = 1$-atom row with $n_2 = 7$-atom second shell [2,3]. Other two-shell or multi-shell cylindrical structures are observed.

The gold LMIS mass spectrum is shown in Figure 2. The largest part of the peaks, and particularly the Au_n^+ species ($n = 1$ to 5) have "normal" intensities which means that they have almost the same intensities as observed in other production of ionized aggregates, for example by the secondary ionic mass spectrometry (SIMS) method [19]. Thus, a large part of ions are certainly produced by direct field emission and the explosion of droplets as it can be verified by looking at their two-peak energy distribution [20]. However the mass spectrum presents an intriguingly wide peak for Au_8^{3+}, absent in SIMS. We can easily verify that the numbers of atoms correspond to the $n_1 + n_2 = 8$ value observed in the forementionned HRTEM and conductance experiments. The strange Au_8^{3+} peak can then be considered as emitted by 8-atom jets.

One may notice that this new emission mode allows us to understand a mass spectrum feature which was inexplicable according to the usual "intensity-stability" rule which explained well the odd-even X_n^+ alternations (X = Cu, Ag, Au) observed in LMIS [21]. Indeed, Au_8^{3+} has a bad stability due to its opened-shell electronic structure and this rule would predict little or no intensity.

Let us now examine if the $\nu = 8$ observed magic radius for monovalent metal nanowires can be explained in a simple way. For these elements, we already know the remarkable results obtained by describing spherical aggregates with a 3-dimension jellium model [22]. The magic numbers given by the model agrees with experimental data. Similarly, one may think that a simple 2-dimension jellium calculation can predict the magic radii of monovalent jets. We use a simple well of potential $U(r) = U_0(r < R_0)$ and $U(r) = 0(r > R_0)$; a n-atom platelet has the radius $r = r_s n^{1/2}$. We take $U_0 = 5$ eV and $r_s = 0.3$ nm which are typical values for heavy noble metals. Our results show that, indeed the increase Δ_n of the D_n electron binding energy ($\Delta_n = D_n - D_{n-1}$), presents relative maxima. The first of them appears for $n = 6$, i.e. close to the $n = 8$ value seen before. The other values given by the calculation are 12, 24, 34. Various improvements can be brought to this model in particularly the use of a more refined potentials.

6 Conclusion

In this paper we have proposed an explanation of some strange features observed in LMIS mass spectra: periodicities for germanium, tin and bismuth, presence of the Au_8^{3+} ion for gold. We have emphasized the role played by the strong electric field at the apex of an operating LMIS which stretches the liquid matter and leads to the formation of thin nanowires with well defined $\nu-$atom sections. The cleavage of these jets by the field explains the observed periodicities (Ge, Sn, Bi) and the presence of Au_8^{3+}.

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