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

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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 ν-atom sections. The Ge^{3+}_{6m+1} and Sn^{3+}_{6m+1}, $m = 3$ to 8, and Ge^{3+}_{6m+4}, $m = 9$ 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^{3+}_{8} ion. ***To cite this article: P. Joyes et al., C. R. Physique 5 (2004).***

Résumé

Nanofils de rayon fini formés dans des sources à évaporation de champ en cours de fonctionnement. Les ions produits par évaporation de champ ont été analysés par spectrographie de masse. Les spectres présentent pour certains éléments des périodicités remarquables, c'est-à-dire des séries de pics équidistants séparés par un nombre d'atomes, ν, constant. Nous montrons que ces particules sont vraisemblablement produites à partir de jets terminés par un cylindre dont la section comporte ν atomes. Les Ge^{3+}_{6m+1} et Sn^{3+}_{6m+1}, avec $m = 3$ à 8, et les Ge^{3+}_{6m+4}, avec $m = 9$ à 14, observés proviendraient ainsi de jets avec $\nu = 6$. Nous examinons aussi le bismuth et l'or. Dans ce dernier cas, le modèle permet d'interpréter la présence encore inexpliquée de l'ion Au^{3+}_{8}. ***Pour citer cet article : P. Joyes et al., C. R. Physique 5 (2004).***

Keywords: Liquid metal ion source; Nanowire; Finite radius; Mass spectrum; Two-dimension jellium

Mots-clés : Source à évaporation de champ ; Nanofils ; Rayon fini ; Spectre de masse ; Jellium à deux dimensions

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Depuis la découverte des nanotubes de carbone [1], des structures analogues, appelées généralement nanofils, ont été observées pour d'autres éléments : or [2,3], platine [4], WS_2 [5], BN [6], Si [7].

Dans cet article, nous montrons que, vraisemblablement, ce type de structure apparaît aussi, pour certains éléments, en émission de champ (LMIS, en anglais) où un champ électrique extrêmement intense (>10 V/nm) est appliqué à une surface conductrice liquide. On explique bien alors les séries de pics équidistants (ν est l'accroissement du nombre d'atomes d'un pic à l'autre) observés dans certains spectres de masse. Ils proviendraient de la fragmentation de nanofils (ou jets) cylindriques dont la section circulaire comporte ν atomes.

Plusieurs arguments généraux peuvent être avancés pour justifier ce point. Des observations faites par microscopie électronique à 3 MeV [8] sur une pointe LMIS de gallium en cours de fonctionnement montrent que des jets extrêmement fins se forment. Des diamètres de 3 nm ont été mesurés. Les modèles théoriques [9,10] conduisent aussi à cet ordre de grandeur.

Le champ électrique très élevé [11] qui règne à la surface du milieu métallique liquide joue un rôle fondamental dans la formation des jets. On sait qu'un milieu métallique fini chargé a tendance à adopter une forme allongée cylindrique sous l'effet des forces électrostatiques. Ce comportement s'étend aux jets apparaissant à la surface d'un liquide conducteur qui vont aussi avoir tendance à s'affiner sous l'effet des mêmes forces. Nous pensons que, pour certains éléments, le diamètre du cylindre décroît en deçà des 3 nm observés pour le gallium, jusqu'à atteindre le domaine des tailles atomiques (typiquement 0,6 nm) où le rétrécissement se fait par marches (Fig. 1).

Pour comprendre comment va se produire l'émission à partir des jets, évoquons les modes d'émission connus en LMIS [12–17]. Dans le cas des ions simplement chargés X_n^+, qui forment l'essentiel du spectre de masse, l'émission se produit soit par émission de champ directe à partir de la surface ou par explosion de gouttes métastables à quelque distance de la surface. Ces deux modes de production sont mis en évidence par l'examen des distributions en énergie des X_n^+ qui présentent deux pics.

On peut prévoir certaines caractéristiques de l'émission à partir de jets cylindriques extrêmement fins comportant ν atomes sur une section. Le rayon de courbure au sommet du jet étant très petit, la densité de charge est élevée et les ions émis emporteront une charge $p+$ importante, $p > 1$. Par ailleurs, la liaison chimique le long de l'axe du jet étant étirée, donc fragilisée, par le champ, le jet va aisément se scinder en tranches de différentes épaisseurs. Si m est le nombre de sections élémentaires, le nombre total d'atomes sera $m\nu$, on observera un ion $X_{m\nu}^{p+}$.

Les expériences menées sur l'étain [13] et le germanium [14] font apparaître des pics X_{6m+1}^{3+}, avec $m = 3$ à 8, qui selon notre modèle correspondraient à des jets comportant $\nu = 6$ atomes sur une section. Dans le cas du germanium une autre série X_{6m+4}^{3+}, avec $m = 9$ à 14, est aussi observée. On note qu'un certain nombre d'atomes, ici 1 puis 4, s'ajoute aux $m\nu$ prévus, cet ajout correspond sans doute à la présence d'un motif de 1 puis de 4 atomes au sommet du jet, emporté lors de l'émission.

La distribution d'énergie de ces ions, qui a été obtenue expérimentalement [16], ne comporte qu'un seul pic. Ceci est en accord avec le mécanisme d'émission proposé. Ces ions, émis initialement au même potentiel que les X_n^+ cités plus haut, arrachés directement par émission de champ, présentent le même type de distribution d'énergie qu'eux.

Des expériences de condensation de Ge_n^+ ou Sn_n^+ en jet d'hélium [18,19] font apparaître des oscillations avec n de certaines propriétés physiques qui ne sont pas cependant aussi nettes que celles que l'on observe ici.

Le spectre de masse du bismuth [15] montre une série de pics Bi_{8m+3}^{3+}, avec $m = 2$ à 5, qui conduit, selon notre modèle, à la présence de jets comportant $\nu = 8$ atomes sur leur section.

On remarquera que l'hypothèse d'une forme cylindrique pour les agrégats de germanium et d'étain est en accord avec la conjecture de Phillips [20–22]. Des calculs plus récents sur Si_n [23] conduisent aussi à des formes allongées qui dans une certaine mesure peuvent s'assimiler à des structures cylindriques. La stabilité relative de ces formes allongées est renforcée dans notre cas par la présence du champ électrique.

Nous proposons une autre structure possible de jet cylindrique composée d'icosaèdres imbriqués.[1]

Nous présentons un spectre de masse expérimental détaillé Fig. 2 qui fait apparaître à la masse Au_8^{3+} un pic bien séparé de Au_2^+ et Au_3^+ et d'intensité intégrée relativement élevée. Cette caractéristique n'apparaît pas dans les références [24,25] où seuls les pics principaux Au^{2+}, Au^+, Au_2^+, Au_3^+, Au_4^+, Au_5^+ sont reportés. Pour ce qui concerne ces derniers la Fig. 2 est en accord avec celle des références [24,25]. Les intensités des pics principaux que l'on observe aussi par d'autres techniques comme l'émission ionique secondaire (SIMS) [25] s'explique bien par la règle « intensité-stabilité ». Or, selon cette règle, l'espèce Au_8^{3+} qui présente une couche électronique ouverte ne devrait pas apparaître. Elle n'est d'ailleurs pas observée en SIMS [26]. Pour ces raisons nous attribuons son existence à la formation de jets ayant $\nu = 8$ atomes sur leur section. Ceci est en accord avec l'observation de nanofils d'or avec $\nu = 8$, par microscopie électronique à haute résolution (HRTEM) [2]. Des expériences de conductance confirment cette valeur [3].

[1] We thank Professor J. Friedel who suggests us this structure.

Nous avons entrepris un calcul par le modèle du jellium à 2 dimensions (ce modèle donne d'excellents résultats à 3 dimensions [27]) qui fournit comme premier rayon magique $\nu = 6$, proche de la valeur observée plus haut. Ce calcul est effectué avec un puits de potentiel carré, l'utilisation d'un modèle plus élaboré devrait conduire à un meilleur accord.

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], WS_2 [5], BN [6], Si [7].

In this Note, we show that similar structures are likely to appear for some elements in operating liquid metal ion sources (LMIS) where a very strong electric field (> 10 V/nm) is applied to a liquid conducting surface. In this case they will rather be called jets. Their presence explains well the series of equidistant peaks (we call ν the increase of the atom number between two successive peaks) observed in some mass spectra. These peaks would come from the fragmentation of cylindrical nanowires (or jets) with a ν-atom circular section.

The Note is presented as follows. We first give, in Section 2, several arguments which lead to thinking that nanowires-like structures may appear in LMIS. In Section 3, we briefly 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 Sections 5 and 6 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 (HV-TEM) observations made by Benassayag, Sudraud and Jouffrey [8] on an operating Ga LMIS shows that extremely thin jets are formed. Diameters of the order of 3 nm were observed. Theoretical models developed by Kingham and Swanson [9] also lead to this order of magnitude. More recently Forbes [10] shows that the main physical points are contained in a relatively simple 3-equation system. The equations express respectively firstly the Bernouilli 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 the experimental data.

Thus, we see that 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. Stabilization 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 [10] when available. They can also be calculated by applying theoretical models [10]. For a large number of elements there is a general agreement between the experimental and theoretical value [11] though some anomalies appear for Al and Au [10]. 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 element.

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 it is well known that elongated shapes are stabilized when they are submitted to an electric field. 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 modelled as in simple finite shapes but, physically, the same conclusion is expected: the jet will elongate and its radius will decrease in order to minimize the electostatic repulsion. If the jet diameter were to decrease as expected from the preceding argument, from the observed 3 nm down to the atomic range, successive discontinuities due to atomic discretization should appear, leading to a shape schematised on Fig. 1.

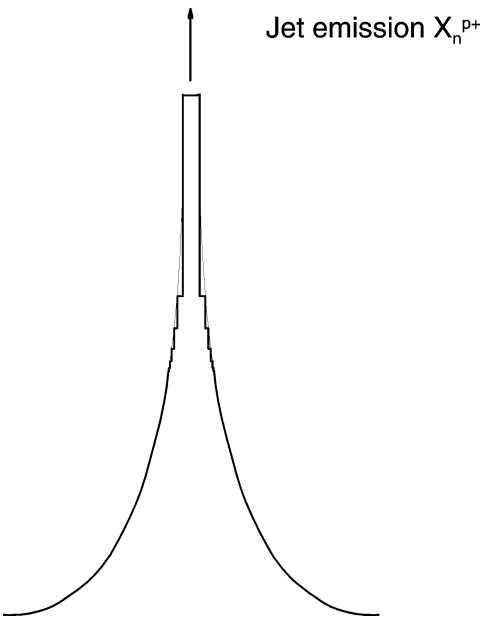

Fig. 1. Schematic representation of a jet shrinking by steps down to the atomic size of the thinnest nanowire.

Fig. 1. Représentation schématique d'un jet se rétrécissant par marche jusqu'à atteindre la dimension atomique du plus petit nanofil possible.

3. Various emission modes

The ion emission from a LMIS has been widely studied by mass spectrometry [12–15]. The energy [16] and angular [17] distributions of the emitted species has 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 from the tip. These two possible X_n^+ origins are revealed by their energy distribution where two peaks are observed [15,16], 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 ($p > 1$).

Now let us come back to experiments on suspended nanowires mentioned before. The modes of formation of these nanowires are diverse. Among them, one may mention the use of a STM (scanning tunnelling microscopy) geometry. In this method the STM tip is dipped into the substrate and then withdrawn. The matter is stretched by the tip and large interatomic spacings appear. In the case of gold for example, distances of 0.3 or 0.4 nm are observed, larger than the bulk nearest-neighbour spacing 0.288 nm [2]. In LMIS cylindrical jets, the strong electric field also stretches the matter and similarly one may expect that the interatomic spacing will increase and the bonding will be 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 [13] and germanium [14] 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 [14]. We notice that additional atoms (1 in the first series; 4 in the second) are present in the emitted aggregates. They could be due to the presence of a cap of atoms at the top of the jet.

Ge_n^+ and Sn_n^+ aggregates ($n \lesssim 70$) are also produced by other experiments, for example by condensation in a helium jet (Ge [18], Sn [19]). Dissociation energies for Ge_n^+ [18] and mobilities for Ge_n^+ and Sn_n^+ [19] are deduced from these data. All

the curves clearly present oscillations versus n, but which have not the same regularity nor the same resolution as in the LMIS results mentioned.

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, t_f, time of flight in the apparatus. For aggregates with $p > 3$ this condition between the lifetimes and t_f would no longer be fulfilled.

The energy distribution of these 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 Section 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 [15] 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 the $\nu = 6$ period and the existence of cylindrical group 4 molecular species is confirmed by a work on Si_n^+ ions. Their reactivity with NH_3 is experimentally studied [20] 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 [21] that these clusters have cylindrical shapes: the aggregates would be the stacking of six-membered rings. A calculation by Jelski et al. [22] shows that, indeed, Si_{36}^+ has a positive charge concentrated at each end and thus can easily react with NH_3 which is nucleophile. For Si_{39}^+ the situation is reverted with negatively charged ends.

More recent calculations on Si_n [23] does not confirm the previous stacking of 6-atom rings, but nevertheless shows that, in a relatively large range of size $19 < n < 26$, prolate geometries, close in some way to cylindrical shapes, present mobilities which agree with measurements. Moreover, the relative stability of these prolate shapes would even be reinforced by the electric field in our case.

Other linear structures should be explored which can also explain the observed 6-atom period, for example a linear stacking of centred icosahedra (13 atoms) where two neighbours share, on the one hand, a 5 atom ring and, on the other hand, one atom which is the centre in one neighbour and a summit in the other. In this case the 6-atom ejected motif would be made of a 5-atom ring capped by one 'central, summit' atom.[2]

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 a $n_2 = 7$-atom second shell [2,3]. Other two-shell or multi-shell cylindrical structures are observed.

We give in Fig. 2 a gold LMIS mass spectrum. Here, our figure gives the spectrum with all its details. We observe between Au_2^+ and Au_3^+ a well isolated wide peak at the Au_8^{3+} mass. We also give the precise shape of the main peaks: Au_n^{2+}, Au^+, Au_3^{2+}, Au_2^+, Au_3^+, Au_4^+, Au_5^+. It can be noted that our results agree with previous LMIS results [24,25] where only the intensities of the main peaks were reported. Other thin peaks also appear in Fig. 2 but none of them present the total integrated Au_8^{3+} intensity. They can be due to impurities or to experimental fluctuations. We consider them as meaningless and do not try to index them. We have also mentioned in Fig. 2 the position of the Au_{16}^{3+} mass where there is a thin peak which should be rejected according to the previous criterium. Consequently the presence of Au_{16}^{3+} is doubtful.

The intensities of the mentioned main peaks can be described by the usual 'intensity-stability' rule. This rule explains well the odd-even X_n^+ alternations observed in LMIS for gold (X = Au [24,25]), or copper and silver (X = Cu, Ag [25]). The same alternation also appears in secondary ion mass spectrometry (SIMS) experiments [26]. Thus, in LMIS, these 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 [24].

What can be said about the intriguingly wide Au_8^{3+} peak? We firstly note that it is absent in SIMS experiments [26] and hence specific to the LMIS process. Moreover we easily verify that the number of atoms correspond to the $n_1 + n_2 = 8$ value observed in the aforementioned HRTEM and conductance experiments. The strange Au_8^{3+} peak can then be considered as emitted by 8-atom jets.

[2] See footnote 1.

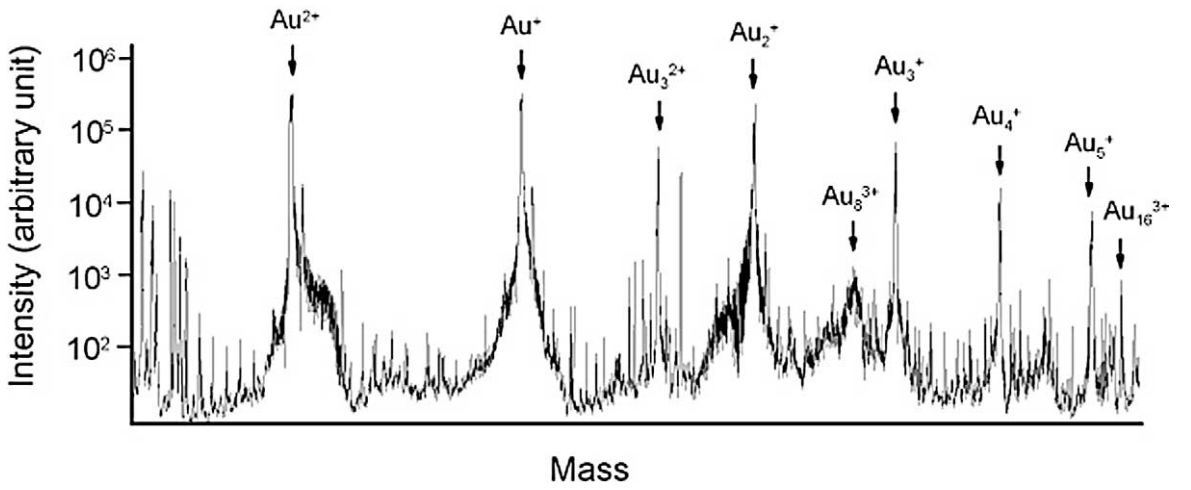

Fig. 2. Gold LMIS mass spectrum. The X_n^+ odd-even alternations mentioned in the text appear for $n > 5$, see for example [23].

Fig. 2. Spectre de masse LMIS de l'or. Les alternances pair-impair des X_n^+ évoquées dans le texte apparaissent pour l'or pour $n > 5$, voir par exemple [23].

One may notice that this new emission mode allows us to understand a mass spectrum feature which was inexplicable according to the 'intensity-stability' rule. Indeed, Au_8^{3+} has a bad stability due to its opened-shell electronic structure and this rule would predict little or no intensity.

6. Simple results of a 2-dimension jellium model

In the same way as we previously discussed whether cylindrical covalent structures were likely for group 4 Ge and Sn elements, let briefly examine the same question for monovalent elements.

As we have seen before, the LMIS jets have extended bonds, and consequently small binding energies, along the field direction supposed to be the cylindrical axis direction. Hence, the stability will be mainly controlled by one atomic section of the cylinder. This platelet can be described by a simple 2-dimension jellium model. Indeed, it is well known that this type of calculation applied to 3-dimension systems, gives remarkable results, for example for spherical monovalent aggregates [27].

In this Note we present the results obtained with a simple $U(r)$ square well potential:

$$U(r) = U_0, \quad 0 \leqslant r \leqslant R_0,$$

$$U(r) = 0, \quad r \geqslant R_0,$$

R_0 is the platelet radius. It is related to the number n of atoms in the platelet by:

$$R_0(n) = r_s n^{1/2}$$

where r_s is the atomic radius. We take $U_0 = 5$ eV and $r_s = 0.3$ nm which are typical values for heavy noble metals.

We solve the Schrödinger equation and derive, for a given n value, the electronic levels spectrum. The levels are filled with n electrons (monovalent metals) and we obtain the total electronic energy D_n.

Our results show that indeed, Δ_n the increase of the D_n electronic 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. Then, it appears that this kind of calculation can be useful to study monovalent jets or nanowires. Various improvements can be brought, in particular by using more refined potential as the Woods–Saxon potential or by taking into account the weak bonding between platelets.

In this Note 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 ν-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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