Element- and Size-Dependent Electron Delocalization in AuₙX⁺ Clusters (X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni)

S. Neukermans, E. Janssens, H. Tanaka, R. E. Silverans, and P. Lievens

Laboratorium voor Vaste-Stoffysica en Magnetisme, K.U.Leuven, B-3001 Leuven, Belgium
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We investigated the stability of gold clusters doped with open 3d-shell atoms (Sc, Ti, V, Cr, Mn, Fe, Co, Ni). Steps, peaks, and odd-even staggering in mass abundance spectra upon photofragmentation provide evidence for enhanced stability for specific cluster sizes. The observed magic numbers are explained in terms of size- and dopant-dependent modifications of the effective mean-field potential within a phenomenological shell-model approach. Element-dependent 3d electron delocalization and odd-even staggering amplitudes are related to the dopant-atom structure.

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The stability of small metallic clusters as a function of size can be described either by models based on shells of electrons in the case of simple alkali and coinage metals or by models based on shells of atoms in the case of more complex metals such as transition metals and rare earths. In alkali and coinage metal clusters, valence electrons are considered to move freely in an effective electrostatic potential resulting from the ionic cores and the other valence electrons. Solving the Schrödinger equation results in discrete energy levels. Their successive filling with itinerant electrons gives rise to a shell structure, and size dependent properties largely are determined by the total number of delocalized electrons [1]. Specifically for gold, both theory and experiment yield evidence for electronic shells with a grouping of levels of the form 1s, 1p, 1d, 2s, 1f, ... (magic numbers 2, 8, 18, 20, 34, ...) [2].

A simple electronic shell model does not suffice to describe the properties of clusters made of more complex metals where most properties, in particular cluster stability, often are discussed in terms of shells of atoms, relating the number of atoms needed to form a compact symmetric structure to an enhanced stability [3]. Still, atomic valence electrons continue to play an essential role in the atom-atom bonding, although the directional bonding of electrons from a partially filled d band prevents the observation of an electronic shell structure.

One way to investigate this interplay between shells of atoms and shells of electrons is to study bimetallic clusters. So far several systems have been investigated, mostly consisting of alkali or coinage metals mixed with a few atoms of more complex (divalent, trivalent, transition) metals. We refer to work on doped alkali clusters [4–7], AlₓXₙ [8], AuₓXₙ⁺ [9, 10], and CuₓZ systems [11] (and references cited therein). Size and composition dependent properties for most of these systems were interpreted taking into account the interplay between the a priori anticipated number of delocalized electrons and structural features deduced from ab initio calculations or ad hoc assumptions [12].

In this Letter we report on photofragmentation experiments on Auₙ⁺ clusters doped with 3d shell transition metal atoms Sc, Ti, V, Cr, Mn, Fe, Co, and Ni. Stability patterns observed in mass abundance spectra will be discussed in terms of simple phenomenological shell-model considerations, emphasizing element and size dependent magic numbers, numbers of delocalized electrons stemming from the dopant, and odd-even alternations.

Beams of bimetallic clusters are produced with a dual-target dual-laser vaporization source [13]. As for the dual source first developed by Kaya and co-workers [14], independent laser pulses are used to evaporate atoms from different targets. Condensation of atoms into clusters is initiated by introducing He gas into the source. Mixed clusters with a wide variety in size and composition can be produced by adjusting well controllable parameters such as ablation laser fluences and the relative timing of gas and laser pulses. Also important is the source geometry, in particular, the distance between the two ablation laser spots, the volume of the condensation chamber, and the nozzle diameter. We used a He gas pressure of 7 bars, vaporization laser intensities of 0.3–0.4 GW/cm², and a conical nozzle (10° opening angle, 1.2 mm diameter).

In photofragmentation experiments the stability of cationic clusters is probed via their relative abundance following multiphoton absorption [10]. The cluster beam is irradiated with high fluence laser light (>2 MW/cm²) stemming from an ArF excimer laser (photon energy 6.43 eV). Photofragments recorded with reflectron time-of-flight mass spectrometry show a size distribution with an enhanced abundance of Auₙ⁺ clusters after photofragmentation, and steps at N = 3, 9, 19, 21, 35, ... correspond to the magic numbers 2, 8, 18, 20, 34, .... Figures 1(b)–1(h) display the intensities of photofragmented Auₙ⁺ X⁺ (X = Sc, Ti, Cr, Mn, Fe, Co, Ni) clusters. In addition to clear drops in abundance after specific cluster sizes, these stability patterns reveal distinct odd-even alternations.
Theoretical studies of unimolecular fragmentation showed that the experimental peak heights $I_N$ relate to the second difference in Helmholtz free energy via

$$\ln\left(\frac{I_N}{I_{N+1}}\right) = \Delta^2 F_N / k_B T,$$

(1)

where $\Delta^2 F_N = 2F_N - F_{N+1} - F_{N-1}$ and $I_N$ is the detected intensity for a cluster with $N$ gold atoms [15]. The quantity defined by Eq. (1) is plotted in Fig. 2 for Au$_N$X$^+$ ($X = $ Au, Cr, Mn, Fe, Co, Ni) as a function of $N$. Assuming that the contribution of fragmentation processes with dopant evaporation can be neglected because of the strong dopant-coincage metal bond strength [11], $\Delta^2 F_N$ can be interpreted as the difference between fragmentation energies of Au$_N$X$^+$, Au$_{N+1}$X$^+$ into a Au atom and Au$_{N-1}$X$^+$, Au$_N$X$^+$, respectively. Positive values of $\Delta^2 F_N$ indicate that the dissociation of Au$_{N+1}$X$^+$ into Au$_N$X$^+$ is more favorable than the fragmentation of Au$_N$X$^+$ into Au$_{N-1}$X$^+$.

Introduction of a dopant-atom in a metal cluster can change its structure and electronic properties significantly. For example, for alkali clusters doped with electronegative elements such as O or C, and for alkali-noble metal binary species, segregation into an ionically bound unit and a metallic part has been observed [9,16–18]. Other bimetallic clusters form alloys where all valence electrons of the constituent atoms are itinerant [7,9,10,17]. The amount of charge transfer, and the existence of ionic-like bonds, can be related to the difference in electronegativity ($\Delta EN$) for both composing elements: ionically bonded subcompounds will exist only for mixed clusters with large $\Delta EN$ [19]. For the binary clusters considered in this work $\Delta EN$ is small [20]; therefore the occurrence of ionic bonds is unlikely, and at most polar bonds may exist.

We will restrict ourselves in this Letter to qualitative discussions within a simple (spherical) shell model, where an ad hoc phenomenological potential, in which all delocalized electrons are confined, is used as an approximation of the electrostatic mean field of the cluster. The unknown shape of this potential evidently depends on size and composition: incorporating (multi-valent) metal atoms in a gold cluster will induce considerable changes, which, e.g., may result in shell inversions. Still, discontinuities in the abundance spectra may be linked to shell closings for (a priori unknown) magic numbers corresponding to the total amount of itinerant electrons in the cluster.

For scandium doped gold clusters intensity drops are observed at Au$_6$Sc$^+$, Au$_{16}$Sc$^+$, and Au$_{32}$Sc$^+$. Assuming that each gold atom delocalizes its 6s electron as for pure gold clusters, these cluster sizes correspond to 8, 18, and 34 itinerant electrons, provided that the Sc atom delocalizes three electrons. Doping with titanium results in discontinuities at Au$_5$Ti$^+$ and Au$_{15}$Ti$^+$, which matches the magic numbers 8 and 18, respectively, if four electrons of the Ti atom contribute to the cluster bonding. This means that for Sc and Ti both the 4s and the 3d electrons are delocalized.
can be considered itinerant, in agreement with investigations of pure Ti clusters [21]. The situation is somewhat different for \( \text{Au}_N \) clusters doped with chromium, manganese, iron, or cobalt. The fragmentation spectra of \( \text{Au}_N\text{Cr}^+ \), \( \text{Au}_N\text{Mn}^+ \), \( \text{Au}_N\text{Fe}^+ \), and \( \text{Au}_N\text{Co}^+ \) clusters feature steps at \( N = 1, 5, 7, 17, (19), \) and 33. These steps correspond to magic numbers 2, 6, 8, 18, (20), and 34 if the dopant contributes two electrons to the cloud of itinerant electrons. In the case of doping with nickel, steps are observed after \( N = 2, 8, \) and 18, suggesting that the Ni atom delivers only one itinerant electron. These findings suggest that for the heavier 3d transition metal atoms delocalization is restricted to the 4s electrons only. Finally for doping with vanadium no prominent shell features are observed. The observed shell features are summarized in Table I. In the present Letter we will focus on three observations: (i) the presence of magic numbers for 6 and 18 delocalized electrons, (ii) the dopant-dependent number of delocalized electrons, and (iii) the different amplitude of the odd-even staggering for different dopant elements.

The enhanced abundance for \( \text{Au}_N X^+ \) \( (X = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \) and \( \text{Co}) \) clusters indicate a very stable structure. Based on foregoing arguments these systems should contain six free electrons, which correspond to an oblate shell closure in the Clemenger-Nilsson model [22]. If there is a good overlap between the optimal electronic structure and a compact geometric ground state, this can lead to a high stability. However, detailed calculations are needed to elucidate the nature of the unusual stability for these specific binary cluster species [23].

While for the heavier dopants the magic numbers fit fairly well to the observations for pure gold clusters, this is not the case for the lighter dopants: the magic number 20 is strongly suppressed or even absent, and 18 manifests itself as a particularly strong shell closure. A similar feature was observed earlier for \( \text{Au}_N X^+ \) \( (X = \text{Al}, \text{Y}, \text{In}) \), and has been related to a modification of the effective mean-field potential by the insertion of a single dopant-atom [9,10]. Assuming a central position of the dopant, its lower electronegativity [19] is likely to cause a bump in the center. This leads to an upward shift of the s valence electron orbitals relative to the orbitals with nonzero angular momentum. Regardless of the exact shape of the potential this will enlarge the gap between the 1d and 2s shells, and decrease the spacing between the 2s and the 1f levels, resulting in exactly the observed features. A similar explanation has been used to account for the appearance of the magic number ten for doped alkali clusters where the higher EN value of the central dopant atoms causes a depression in the potential well, pulling the 2s orbital below 1d [7,17].

The dependence of the number of added itinerant electrons on the kind of dopant can be accounted for by differences in the spatial extent of the occupied \( d \) orbitals. The large size of the \( d \) electron wave functions of metals at the beginning of the \( 3d \) series (Sc, Ti) [11] results in a strong hybridization with the Au electron orbitals. For example, the Ti \( 3d \) orbitals are delocalized and fully participate as valence orbitals in the chemical bonding of Ti clusters [21]. For \( \text{Au}_N X^+ \) \( (X = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}) \), the \( 3d \) orbitals are spatially confined at the impurity, and mainly s electrons contribute to the metallic bonding.

The odd-even staggering (OES) in the stability pattern of pure \( \text{Au}_N^+ \) clusters [Figs. 1(a) and 2(a)] reflects that clusters with an even number of delocalized electrons are more stable. The OES is due to structural deviations from spherical symmetry: breaking the symmetry of the mean

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**TABLE I.** Observed shell features. Intensity drops in the abundance pattern occur after \( \text{Au}_N X^+ \). \( n_v \) is the number of delocalized electrons stemming from the dopant, and \( n_e \) denotes the total number of delocalized electrons, corresponding with the observed steps.

<table>
<thead>
<tr>
<th>( X )</th>
<th>Valence</th>
<th>( N )</th>
<th>( n_v )</th>
<th>( n_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>( 4f^{14}5d^{10}6s^1 )</td>
<td>3, 9, 19, 21, 35</td>
<td>1, 2, 8, 18, 20, 34</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>( 3d^24s^2 )</td>
<td>6, 16, 32</td>
<td>3, 8, 18, 34</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>( 3d^24s^2 )</td>
<td>5, 15, (27)</td>
<td>4, 8, 18, (30)</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>( 3d^24s^2 )</td>
<td>5, 7</td>
<td>22, 6, 8</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>( 3d^44s^1 )</td>
<td>1, 5, 7, 17, (19), 33</td>
<td>2, 6, 8, 18, (20), 34</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>( 3d^44s^2 )</td>
<td>1, 5, 7, 17, (19), 33</td>
<td>2, 6, 8, 18, (20), 34</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>( 3d^64s^2 )</td>
<td>1, 5, 7, 17, (19), 33</td>
<td>2, 6, 8, 18, (20), 34</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>( 3d^74s^2 )</td>
<td>1, 5, 7, 17, (19), 33</td>
<td>2, 6, 8, 18, (20), 34</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>( 3d^84s^2 )</td>
<td>2, 8, 18</td>
<td>1, 2, 8, 18</td>
<td></td>
</tr>
</tbody>
</table>
field induces single-particle orbitals to be deformed [24]. This deformation removes the angular momentum degeneracy within one shell, leaving just the spin degeneracy of each level. We expect to observe an OES in the abundance pattern of all clusters that can be described by deformed shell models. A priori, there is no obvious reason why the amplitude of the OES in Au$_N$X$^+$ clusters should be strongly dopant dependent. Nevertheless, Figs. 1 and 2 show that the OES is pronounced for Au$_N$Sc$^+$, Au$_N$Ti$^+$, and Au$_N$Mn$^+$ clusters, while the effect is much weaker for Au$_N$Cr$^+$ and Au$_N$Fe$^+$ clusters, and almost absent for Au$_N$V$^+$, Au$_N$Co$^+$, and Au$_N$Ni$^+$. Below follows a qualitative explanation of this effect, relating the amplitude of the odd-even fluctuations to differences in the atomic structure of the dopants.

Because of the near degeneracy of the 3$d$ and 4$s$ energy levels in transition metal atoms, the promotion energy from 3$d^44$s$^2$ to 3$d^{10}4$s$^1$ atomic electron structures is small. Introducing a transition metal atom in a matrix such as a Au$_N$ cluster, results in a shift of the absolute energies of all atomic configurations. If the promotion energy is small enough, this shift may lead to an inversion of the lowest atomic state between 3$d^44$s$^2$ to 3$d^{10}4$s$^1$. Such inversion may be the reason why Cr behaves divalent in a Au matrix and Ni monovalent (as opposed to, respectively, the 3$d^54$s$^1$ and 3$d^84$s$^2$ atomic ground state configurations). This delicate energy balance between the 3$d^44$s$^2$ and 3$d^{10}4$s$^1$ configurations likewise could explain the dopant dependence of the amplitude of the OES in those Au$_N$X$^+$ clusters where only the 4$s$ electrons of the impurity are delocalized. If this promotion energy would be comparable to the energy gain responsible for the stability enhancement for clusters with even $n_e$, both contributions would cancel out. The electronic configuration of the dopant will match a 3$d^44$s$^2$ or a 3$d^{10}4$s$^1$ structure, depending on the number of gold atoms in the cluster, $N$, in a way that the total number of delocalized electrons ($N+1$ or two 4$s$ electrons) always is even. The promotion energies of the dopant atoms are inserted in Fig. 2, and a striking positive correlation between the atomic promotion energy and the amplitude of the OES can be noticed. The same energetic competition between different effects also may be the reason for the inversion of the OES for Au$_N$Ni$^+$. If the Ni 3$d^84$s$^2$ electronic configuration is favored, this results in six delocalized electrons which for other doped Au clusters is a magic number. Another experimental observation in accordance with the subtle balance between monovalent and divalent character of the dopants is the smeared-out intensity jump at Au$_{33}$Co$^+/Au_{34}$Co$^+$. For Co the atomic promotion energy is small, such that both Au$_{33}$Co$^+$ and Au$_{34}$Co$^+$ may contain an even number of 3$d$ delocalized electrons.

In conclusion, stability patterns of photofragmented Au$_N$X$^+$ ($X =$ Sc, Ti, V, Cr, Mn, Fe, Co, Ni) clusters obviously reflect a shell structure, with dopant-dependent magic numbers. The lightest 3$d$ elements (Sc, Ti) delocalize their 4$s$ and 3$d$ electrons, while for the heavier 3$d$ elements (Cr, Mn, Fe, Co, Ni), only 4$s$ electrons are delocalized. The strongly dopant-dependent amplitude of the odd-even abundance staggering is explained as due to a cluster size dependent number of delocalized electrons which can be related to the energy difference between a 3$d^44$s$^2$-like and a 3$d^{10}4$s$^1$-like electronic configuration of the impurity.

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*Electronic address: Peter.Lievens@fys.kuleuven.ac.be

[19] An often used criterion states that ionic bonds exist if $\Delta EN > 1.7$. Following the Pauling scale of electronegativity (see, e.g., http://www.webelements.com), $\Delta EN$ equals 2.65 and 1.75, respectively, for Cs$_2$O$_M$ and Cs$_2$Au$_M$ where ionic subcompounds exist [16,17]. No ionic bonds were considered for the mixed clusters Al$_x$Au$_M$ ($\Delta EN = 0.93$), Na$_x$Au$_M$ ($\Delta EN = 1.61$), and Na$_x$Zn$_M$ ($\Delta EN = 0.72$) [7,9,10,17].
[20] Using the Pauling scale $\Delta EN$ ranges from 0.63 to 1.18 for Au$_N$X$_M$ with $X =$ Sc, Ti, V, Cr, Mn, Fe, Co, Ni.