Element- and Size-Dependent Electron Delocalization in $Au_N X^+$ 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 (Received 3 May 2002; published 24 January 2003)

We investigated the stability of gold clusters doped with open 3*d*-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 3*d* 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, $1p, 1d, 2s, 1f, \dots$ (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], AI_NX_N [8], Au_NX_M [9,10], and $Cu_{12}X$ 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 Au_N clusters doped with 3*d* 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 shellmodel 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 dualtarget 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 timeof-flight mass spectrometry show a size distribution with an enhanced abundance of Au_N^+ clusters after photofragmentation, and steps at $N = 3, 9, 19, 21, 35, \ldots$ correspond to the magic numbers 2, 8, 18, 20, 34, Figures 1(b)-1(h) display the intensities of photofragmented Au_NX^+ (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 oddeven alternations.



FIG. 1. Abundances of fragmented $Au_N X^+$ clusters as a function of the number of gold atoms in the cluster, for X = Au (a), Sc (b), Ti (c), Cr (d), Mn (e), Fe (f), Co (g), Ni (h).

Theoretical studies of unimolecular fragmentation showed that the experimental peak heights I_N relate to the second difference in Helmholtz free energy via

$$\ln(I_N/I_{N+1}) = \Delta_2 F_N/k_B T, \tag{1}$$

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-coinage 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 $Au_N X^+$ into $Au_N X^+$ into $Au_N X^+$ into $Au_N X^+$ into $Au_N X^+$.

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 (ΔEN) for both composing elements: ionically bonded subcompounds will exist only for mixed clusters with large ΔEN [19]. For the binary clusters considered in this work ΔEN 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 (multivalent) 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_6Sc^+ , $Au_{16}Sc^+$, and $Au_{32}Sc^+$. Assuming that each gold atom delocalizes its 6*s* 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_5Ti^+ 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 4*s* and the 3*d* electrons



FIG. 2. $\ln(I_{N+1}/I_N) = \Delta_2 F(N)/k_B T$ with I_N the abundance of $\operatorname{Au}_N X^+ [X = \operatorname{Au}(a), \operatorname{Cr}(b), \operatorname{Mn}(c), \operatorname{Fe}(d), \operatorname{Co}(e), \operatorname{Ni}(f)]$, plotted as a function of N. ΔE_p is the promotion energy from a $3d^{x}4s^2$ to a $3d^{x+1}4s^1$ atomic electron configuration, * means that the ground state has a $3d^{x+1}4s^1$ electron configuration.

can be considered itinerant, in agreement with investigations of pure Ti clusters [21]. The situation is somewhat different for Au_N clusters doped with chromium, manganese, iron, or cobalt. The fragmentation spectra of Au_NCr^+ , Au_NMn^+ , Au_NFe^+ , and Au_NCo^+ 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 Au_5X^+ (X = V, Cr, Mn, Fe, and 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

TABLE I. Observed shell features. Intensity drops in the abundance pattern occur after Au_NX^+ . 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.

X	Valence	N	n_v	n _e
Au	$4f^{14}5d^{10}6s^{1}$	3, 9, 19, 21, 35	1	2, 8, 18, 20, 34
Sc	$3d^{1}4s^{2}$	6, 16, 32	3	8, 18, 34
Ti	$3d^24s^2$	5, 15, (27)	4	8, 18, (30)
V	$3d^34s^2$	5, 7	2?	6, 8
Cr	$3d^54s^1$	1, 5, 7, 17, (19), 33	2	2, 6, 8, 18, (20), 34
Mn	$3d^54s^2$	1, 5, 7, 17, (19), 33	2	2, 6, 8, 18, (20), 34
Fe	$3d^{6}4s^{2}$	1, 5, 7, 17, (19), 33	2	2, 6, 8, 18, (20), 34
Co	$3d^{7}4s^{2}$	1, 5, 7, 17, (19, 33)	2	2, 6, 8, 18, (20, 34)
Ni	$3d^{8}4s^{2}$	2, 8, 18	1	2, 8, 18

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 $Au_N X^+$ (X = Al, Y, In), and has been related to a modification of the effective mean-field potential by the insertion of a single dopantatom [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 1dand 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 3*d* series (Sc, Ti) [11] results in a strong hybridization with the Au electron orbitals. For example, the Ti 3*d* orbitals are delocalized and fully participate as valence orbitals in the chemical bonding of Ti clusters [21]. For Au_NX⁺ (X = Cr, Mn, Fe, Co, Ni), the 3*d* 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 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

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_NX^+ clusters should be strongly dopant dependent. Nevertheless, Figs. 1 and 2 show that the OES is pronounced for Au_NSc^+ , Au_NTi^+ , and Au_NMn^+ clusters, while the effect is much weaker for Au_NCr^+ and Au_NFe^+ clusters, and almost absent for Au_NV^+ , Au_NCo^+ , and Au_NNi^+ . 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 3d and 4s energy levels in transition metal atoms, the promotion energy from $3d^{x}4s^{2}$ to $3d^{x+1}4s^{1}$ 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 $3d^{x}4s^{2}$ to $3d^{x+1}4s^{1}$. Such inversion may be the reason why Cr behaves divalent in a Au matrix and Ni monovalent (as opposed to, respectively, the $3d^54s^1$ and $3d^84s^2$ atomic ground state configurations). This delicate energy balance between the $3d^{x}4s^{2}$ and $3d^{x+1}4s^{1}$ configurations likewise could explain the dopant dependence of the amplitude of the OES in those $Au_N X^+$ clusters where only the 4s 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 $3d^{x}4s^{2}$ or a $3d^{x+1}4s^{1}$ structure, depending on the number of gold atoms in the cluster, N, in a way that the total number of delocalized electrons (N+ one or two 4s 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 Au₅Ni⁺. If the Ni $3d^84s^2$ 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 34 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) delo-

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calize their 4s and 3d electrons, while for the heavier 3d elements (Cr, Mn, Fe, Co, Ni), only 4s 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 $3d^{x}4s^{2}$ -like and a $3d^{x+1}4s^{1}$ -like electronic configuration of the impurity.

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

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