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${M@Au_{16}^-}$ ($M=\text{Fe,Co,Ni}$)

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Magnetic doping of the golden cage cluster $M @ \text{Au}_{16}$ ($M=\text{Fe,Co,Ni}$)

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Structural, electronic, and magnetic properties of the golden cage doped with a transition-metal atom, $M\text{Au}_{16}^-$ ($M=\text{Fe,Co,Ni}$), are investigated using trapped ion electron diffraction, photoelectron spectroscopy, and density-functional theory. The best agreement to experiment is obtained for endohedral $M @ \text{Au}_{16}^-$ structures but with considerable distortions to the parent $\text{Au}_{16}^-$ cage. Fe@Au$_{16}$ and Co@Au$_{16}$ are found to have similar structures with $C_3$ symmetry while a $C_1$ structure is obtained for Ni@Au$_{16}^-$. The 4$s$ electrons are observed to transfer to the Au$_{16}$ cage, whereas atomiclike magnetism due to the unpaired 3$d$ electrons is retained for all the doped clusters.

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The local magnetic properties of dilute magnetic impurities in nonmagnetic hosts have been addressed with great experimental and theoretical efforts in the past decades. 1–7 Atomic clusters provide a unique medium for exploring local magnetism as the cluster size, the number of valence electrons, and the local structures can be readily controlled and varied. 8–11 In particular, a single magnetic atom trapped in a metallic cage would be an interesting system and an ideal molecular model for dilute magnetic alloys. 12–19 The Au$_{16}$ cluster has been found recently to possess a hollow cage structure with a slightly distorted tetrahedral ($T_d$) symmetry, 20 which has a sufficiently large internal volume to encapsulate a foreign atom to form endohedral clusters. Several theoretical and experimental studies have been recently reported on doped Au$_{16}$ clusters. 21–28 Both endohedral and exohedral dopings have been observed, and the structures of doped Au$_{16}$ clusters are found to be determined by the nature of the dopant-Au interactions. Here we report a study on doping the Au$_{16}^-$ cage with transition-metal atoms, $M\text{Au}_{16}^-$ ($M=\text{Fe,Co,Ni}$). We found that the three magnetic atoms are all doped inside the golden cage but with significant distortions to the parent cage structure. The dopant atoms maintain their atomiclike $d$ configurations in $M @ \text{Au}_{16}$, while their 4$s$ electrons can be viewed as transferred to the golden cage.

We use trapped ion electron diffraction (TIED), photoelectron spectroscopy (PES), and density-functional theory (DFT) calculations in the current study. The TIED technique probes the atomic structures of size-selected cluster ions. 29 Its potential has been demonstrated by a series of recent works on the structures of silver and gold cluster ions over a wide size range. 30–34 PES is a powerful technique to probe the electronic structure of size-selected clusters. The combination of these experimental techniques with DFT calculations affords a comprehensive understanding of the structural, electronic, and magnetic properties of the transition-metal-atom-doped golden cages.

The bimetallic cluster anions $M\text{Au}_{16}^-$ ($M=\text{Fe,Co,Ni}$) were produced either by a magnetron sputtering source for TIED or by a laser vaporization source for PES using composite $M/\text{Au}$ target disks. In the TIED experiment, about $10^5$–$10^6$ size-selected cluster anions are stored in a radio frequency quadrupole ion trap and thermalized through collisions with a He buffer gas to a temperature of 100 ± 2 K. The ion cloud is then irradiated by an electron beam (40 keV, approximately 1–2 μA). Diffraction electrons from the clusters are detected by a phosphor screen assembly and integrated on a charge-coupled device (CCD) camera. The scattering pattern is background corrected and converted into a modified molecular scattering intensity as a function of momentum transfer. This function is then compared to simulated scattering functions based on DFT candidate structures. A quantitative measure of the agreement between experimental and simulated scattering functions is expressed in a weighted profile factor $R_w$. 32 Further details of the experimental configuration and data analysis are given elsewhere. 23–34

The PES experiment was performed using a magnetic-bottle PES apparatus equipped with a laser vaporization supersonic cluster source. 35 Negatively charged clusters were extracted from the cluster beam and analyzed using a time-of-flight mass spectrometer. The $M\text{Au}_{16}$ clusters were selected and decelerated before being photodetached by a 193 nm laser beam from an ArF excimer laser. The photoelectron spectra were calibrated using the known spectrum of Au$^-$. The electron kinetic-energy resolution of the apparatus was $\Delta E/E \sim 2.5\%$.

In the theoretical study, we performed extensive structural searches using the basin-hopping algorithm 36 combined with DFT structural optimization. 37–38 The generalized-gradient approximation in the Perdew-Wang (PW91) functional form, implemented in the Vienna $ab$ initio simulation package (VASP), 39 was used for the DFT calculations. 40 Specifically, the cutoff energy for the plane-wave expansion was 236 eV and the Brillouin zone was sampled with $\Gamma$ point only. Periodic boundary conditions were employed in all three directions, whereas the dimension for the cubic supercell was $15 \times 15 \times 15$ Å$^3$. Typically, after 200–300 basin-hopping steps, a few tens of structurally distinct anion isomers were generated. These isomers were reoptimized using another DFT method, namely, the Perdew-Burke-Ernzerhof functional 41 with a scalar relativistic effective core potential and the cutoff energy for the plane-wave expansion was 236 eV and the Brillouin zone was sampled with $\Gamma$ point only. Periodic boundary conditions were employed in all three directions, whereas the dimension for the cubic supercell was $15 \times 15 \times 15$ Å$^3$. Typically, after 200–300 basin-hopping steps, a few tens of structurally distinct anion isomers were generated. These isomers were reoptimized using another DFT method, namely, the Perdew-Burke-Ernzerhof functional 41 with a scalar relativistic effective core potential and...
LANL2DZ basis set implemented in the GAUSSIAN03 package. Single-point energies of the corresponding neutral isomers in the anion geometries were then calculated to evaluate the first vertical detachment energy (VDE) of the anion isomers. The binding energies of deeper orbitals were added to the first VDE to give the VDEs of the excited states. Each calculated VDE was fitted with a Gaussian of width 0.04 eV to yield the simulated PES spectra.

Our global minimum search found many low-lying isomers close in energy and with subtle structural differences. Figure 1 displays the TIED data fitted using the best candidate structures for \( MAu_{16} \) (\( M=\text{Fe,Co,Ni} \)) that also agree well with the PES data, as will be discussed below. For \( FeAu_{16} \), the lowest energy structure is of \( C_2 \) symmetry (Fig. 1), which is endohedral in nature but with some appreciable distortion to the parent tetrahedral (\( T_d \)) \( Au^- \) cage. Of all the low-lying structures the simulated scattering function of the \( C_2 \) isomer fits the TIED data best (\( R_w=2.7\% \)). The endohedral structure with \( T_d \) symmetry shows a much larger \( R_w \) value (8.0\%) and can be ruled out as a major contributor to the cluster ensemble probed. Nevertheless, a small contribution from the \( T_d^- \)-like structure is possible because a mixture fit by adding ~20\% \( T_d \) isomer leads to a slight improvement in the \( R_w \) value (2.0\%). The lowest energy structure found for \( CoAu_{16} \) is very similar to \( FeAu_{16} \), i.e., a \( C_2 \) structure (Fig. 1), which is among the structures giving the best fit (\( R_w=3.3\% \)) to the TIED data. However, several other low-lying endohedral structures can also fit the TIED data well. In particular, a \( C_1 \) structure (0.13 eV higher in energy) similar to \( NiAu_{16} \) (see below) gives a very good \( R_w \) value of 2.8\%. Contributions from different isomers are also probable because mixtures of the \( C_2 \) or the \( C_1 \) structure with the \( T_d \) structure in the ratio of 0.7/0.3 or 0.8/0.2 lead to improved \( R_w \) values of 2.5\% or 2.0\%, respectively. However, we assign the \( C_2 \) isomer as the main contributor for \( CoAu_{16}^- \) because it is the lowest energy structure from our calculation and it also gives better agreement with our PES data (see below). For \( NiAu_{16}^- \), the structure giving the best agreement between experimental and simulated scattering functions is a \( C_1 \) structure (\( R_w=2.4\% \)), as shown in Fig. 1. The \( C_2 \) structure similar to \( FeAu_{16} \) or \( CoAu_{16} \) gives an \( R_w \) of 3.4\% and a mixture fit of both does not significantly reduce the \( R_w \) value. Both structures are slightly higher lying isomers, 0.10 and 0.14 eV, respectively, above the lowest energy structure, which can be ruled out as a major component because of its high \( R_w \) value (9.1\%). Again the tetrahedral cage structure (\( R_w=11\% \)) can be ruled out as a major contributor.

The above structure assignments are corroborated and complemented by comparison between the experimental and simulated PES spectra. Figure 2 shows the experimental PES spectra of \( MAu_{16}^- \) (\( M=\text{Fe,Co,Ni} \)) at 193 nm. The spectra of \( FeAu_{16} \) and \( CoAu_{16} \) are similar, both featuring a low binding energy peak at \( -3 \) eV (X) followed by an energy gap, a group of well-resolved peaks between 4 and 5 eV, and more congested Au 5d band beyond 5.5 eV. The spectrum of \( NiAu_{16} \) is very different and much more congested in the low binding energy range compared to that of \( FeAu_{16} \) and \( CoAu_{16}^- \), suggesting that the structure of \( NiAu_{16} \) may also be very different as born out from the above comparison of TIED and DFT calculations. The PES spectra all seem to contain weak diffuse signals, more clearly in the cases of \( FeAu_{16} \) and \( CoAu_{16} \) following the X band [Figs. 2(a) and 2(b)], which may come from weakly populated isomers consistent with the TIED data. The first VDE for \( MAu_{16}^- \) is given in Table I.

It is informative to compare the current PES data with those of \( CuAu_{16} \) and \( ZnAu_{16} \). Both Cu and Zn have a closed 3d shell and the doped clusters possess endohedral structures with little distortion to the parent golden cage. Cu@\( Au_{16} \) is a closed-shell 18-electron system, in which the Cu 4s electron is transferred to the gold cage and it can be
viewed as Cu$^+ @ Au_{16}^{2−}$. The low binding energy range of its PES spectrum between 4 and 5 eV consists of a characteristic three-peak feature due to the $t_2$ and $e$ valence molecular orbitals in the $T_d$ cluster.$^{21}$ Zn@Au$_{16}^{-}$ is a 19-electron system, in which the two 4s electrons of Zn are transferred to the golden cage. The extra electron in the anion enters a new electron shell, resulting in a low binding energy feature much separated from the three-peak feature derived from the $t_2$ and $e$ orbitals. The PES spectra of FeAu$_{16}^{-}$ and CoAu$_{16}^{-}$ are reminiscent of the Zn@Au$_{16}^{-}$ spectrum. In particular, the low binding energy peak ($X$) and the ensuring energy gap are very similar to what was observed in the spectrum of Zn@Au$_{16}^{-}$, suggesting that the two 4s electrons of Fe(3$d^4$4$s^2$) and Co(3$d^7$4$s^2$) are also transferred to the golden cage and the extra electron in the anion enters in a new electron shell on the golden cage. The more complex spectral features between 4 and 5 eV suggest structural distortions to the parent cage, as well as possible contributions from the open 3$d$ shell. The more complex PES spectrum of NiAu$_{16}^{-}$ suggests a much more significant distortion to the parent gold cage. In particular, the missing low binding energy peak [Fig. 2(e)] implies that the extra electron in the NiAu$_{16}^{-}$ anion enters a 3$d$ orbital rather than a new shell on the gold cage, most likely due to the fact that in Ni the 3$d^8$4$s^2$ and 3$d^9$4$s^1$ configurations are nearly degenerate. All the above PES observations are consistent with the structural information derived from the TIED data.

The simulated PES spectra for $M @ Au_{16}$ (Fig. 3) support the above interpretations and allow a better understanding of the experimental data. For FeAu$_{16}^{-}$ among several low-lying isomers, the simulated spectrum of the $C_2$ structure [Fig. 3(a)] agrees best with the experimental spectrum. Specifically, the weak peak observed at $\sim 3.7$ eV [Fig. 2(a)] in the gap region is well reproduced in the simulated spectrum by an Fe 3$d$ derived band [Fig. 3(a)]. The first detachment band is indeed due to a Au 6$s/6$p type orbital [also see the inset of Fig. 3(a)], similar to that in Zn@Au$_{16}^{-}$. For CoAu$_{16}^{-}$, several low-lying isomers give similar simulated spectra, but the $C_2$ structure [Fig. 3(b)] gives the best overall fit to the experimental PES data. Similar to Fe@Au$_{16}$ and Zn@Au$_{16}^{-}$ the first PES feature in CoAu$_{16}^{-}$ is also due to a Au 6$s/6$p derived orbital [see the inset of Fig. 3(b)]. For NiAu$_{16}^{-}$ only the $C_4$ structure gives a simulated spectrum [Fig. 3(c)], which agrees well with the experiment, validating the TIED structural assignment. Importantly, the first detachment feature from NiAu$_{16}^{-}$ indeed comes from a Ni 3$d$ derived orbital, as shown in the inset of Fig. 3(c). The calculated first VDE is also in good agreement with the experimental data, as compared in Table I. Overall, the comparison of the simulated and experimental PES results lends considerable further support to the structures obtained for the three transition-metal-doped golden cages. The transition-metal dopants are clearly endohedral in nature, albeit the parent golden cage is significantly distorted, in particular, in the case of Ni.

Previous studies show that the dopant-Au interactions are critical in determining the structures of the doped golden cages. Cu and Zn, which have closed 3$d$ shells, primarily donate their 4$s$ electrons to the cage, forming charge-transfer complexes with very little distortions to the cage.$^{23,28}$ Dopants, such as Si or W, have strong interactions with Au and they distort the golden cages and form other new types of structures.$^{24−26}$ The open 3$d$ shells for Fe, Co, and Ni suggest that they may have more significant interactions with Au, leading to the observed structural distortions in the doped $M @ Au_{16}$ clusters. Indeed, the decomposed density-of-states spectra in Fig. 3 show that the 3$d$ orbitals of the dopant atoms have considerable hybridization with the host golden cage. This is particularly pronounced for Ni@Au$_{16}^{-}$ consistent with its much distorted $C_4$ structure, in which the Ni atom appears to move to one side of the cage and interacts with fewer Au atoms (Fig. 1).
Interestingly, although there is considerable interaction between the transition-metal atoms and the host gold cage, the 3d states of the dopant atoms remain largely localized and the atomiclike magnetism is maintained in the doped clusters. We found that Fe@Au_{16} (M=6) and Co@Au_{16} (M=5) have high spins, while Ni@Au_{16} has a lower spin (M=2), consistent with the stronger Ni-cage interactions. Mulliken atomic spin density analyses show that the spin densities are mainly located on the central dopant atom for all three doped clusters. The bonding in the doped cluster anions can be viewed as an Au_{16}− interacting with a Fe^{2+}/Co^{2+} core or Au_{16}− interacting with a Ni^{2+} core. The neutral M@Au_{16} clusters can all be described as M^{2−}@Au_{16} (M=Fe, Co, Ni), where the two 4s electrons are transferred to the cage and the dopant possesses d^5, d^6, and d^8 valence configurations, respectively, exactly like that in the atoms. Thus, the current work shows that the Au_{16} hollow cage provides a much more flexible host to protect the spins of the dopant atom. We anticipate that many other transition-metal atoms may be doped into the golden cage and maintain their local magnetic moments, forming a new class of endohedral golden cage clusters with varying magnetic properties.

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