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Autor(en): **Châtelain, A.**

Objekttyp: **Article**

Zeitschrift: **Helvetica Physica Acta**

Band (Jahr): **62 (1989)**

Heft 6-7

PDF erstellt am: **19.09.2024**

Persistenter Link: https://doi.org/10.5169/seals-116067

Helvetica Physica Acta
Vol. 62 (1989)

0018-0238/89/070706-04$1.50+0.20/0

METALLIC CLUSTERS OF ATOMS AND SMALL PARTICLES : SOME STRUCTURAL AND ELECTRONIC PROPERTIES

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Extended abstract :

The Physics of clusters of atoms and of small particles is now a well established domain between that of the atomic and molecular physics and that of the conventional solid state physics. Studies of these intermediate systems are important not only from a fundamental point of view but also from the point of view of applications (chemisorption, catalysis, nucleation processes, powder metallurgy, etc...) Experiments are now performed on size selected beams of clusters (neutral or charged) using optical techniques, photo-electron spectroscopy, magnetic or dielectric responses, etc... The more traditional approach of small particles supported on a surface or embedded in a matrix is still very much active, despite the presence of size distributions, because of the applications and also because of the importance of the temperature dependences of many phenomena.

We present here a summary of some of the recent experimental results obtained in the Institut de Physique Expérimentale of EPFL.

It is now well established that metal clusters such as Na, K, Au, Ag exhibit shell structure of single electron levels with spherical shell closings occuring at 8, 20, 40 .... valence electrons **[1]**. Recently, collective oscillations have been observed using photoabsorption cross section measurements **[2]**. This cluster spectroscopy with the addition of static electric polarizability measurements is a particularly efficient tool to detect electronic property changes with cluster size. Neutral Al clusters of atoms have been prepared in a beam using laser vaporization source. Due to their static polarizability, the clusters

are deflected in an inhomogeneous DC electric field. The experimental setup is characterized by a novel position sensitive time of flight detection. The experimental results show that a transition from non metallic to metallic behavior take place in Al when the size increases [3].

It is of interest to understand the stability and metastability of multiply charged metal clusters. From elementary considerations, there exists a critical cluster size $n_c(z)$ below which the Coulomb energy of the total charge z exceeds the cluster binding energy. Early experiments suggested this size could be observed directly in cluster mass spectra, with clusters smaller than $N_c(z)$ rendered unobservable by their spontaneous decay. However, the many observations of clusters well below predicted critical sizes, indicate that such a simple picture of multiply charged clusters may be incomplete. Therefore, charge-exchange and fragmentation cross-section measurements on Au_2^{2+}, Au_3^{2+}, Au_4^{2+}, and Au_4^{3+} have been performed [4]. Limits on the cluster electron affinities are obtained in terms of the ionization energies of Ar, N_2, Kr, CO, Xe, and O_2. The measurements have been carried out in a tandem triple-quadrupole mass spectrometer on clusters produced by a liquid-metal ion source. In the tandem mass spectrometer the first quadrupole selects a particular M/z for experimentation. The clusters interact with the target gas in the second quadrupole, which is operated as a nonselective ion guide. The third mass spectrometer analyzes the charge-exchange and fragmentation products. Ion kinetic energies are typically 10 eV. Fragmentation cross sections, largely independent of the gas species, are comparable to those for charge exchange. The metastability of Au_2^{2+} is shown to be implied by the lower bound on its electron affinity. These experimental results are in agreement with recent theoretical work done partly in our Institute [5].

The various structures of small gold particles deposited onto an amorphous surface have been determined using high resolution electron microscopy observations compared with calculated images using the multislice method [6], [7]. Although simulated for

ideal packings of atoms, computer image lead to the qualitative identification of many existing structures among gold particles : regular fcc cubooctahedron and multiply twinned particles icosahedron and decahedron. They clearly explain the origin of the observed contrasts and show HREM imaging artefacts. In the case of icosahedral particles, the agreement with observations is very good for images along a threefold symmetry axis. For the fivefold symmetry, the computed contrasts explain some anomalous features.

Electron diffraction has been performed on ultrafine unsupported silver particle in a molecular beam of He carrier gas **[8]**. The diffraction patterns obtained indicate clearly a change from fcc structure at larger sizes to MTP structure below 4 nm. Icosahedral and decahedral structure co-exist in the beam and are thus an intrinsic property not due to the presence of a sample holder.

Samples of small Pt particles (a few nanometer in diameter) supported on slightly bigger grains of TiO_2-anatase have been studied by Nuclear Magnetic Resonance **[9]**, **[10]**. A combination of Knight shift (K) and relaxation time (T_1) measurements allows a quantitative interpretation in terms of the local densities of states (LDOS) at the Fermi energy for the s-like and d-like electrons. The definite metallic character of the Pt particles is evidenced by the Korringa relationship. A description establishes the correspondence : $(K, T_1) \rightarrow (D_s (E_F), D_d (E_F))$. A depleted Fermi LDOS is found along with a significant de-enhancement of the clean surface with respect to the bulk, due essentially to d-electrons. Hydrogen adsorbate induces modification of the surface Fermi LDOS at E_F which is further diminished compared to the clean one. The NMR results on "clean" particles are not in agreement with the so-called "quantum size effects" predictions. This is due in particular to the local densities of state at the Fermi energy which show considerable site dependence when going from the surface to the interior of the particle.

In order to have size selected metal clusters in rare gas matrices or on a solid surface, a new apparatus has been constructed **[11]**. Metal cluster cations, produced by Ar^+ sput-

tering, are energy analyzed and then mass selected in a quadrupole mass filter. The clusters are neutralized by low energy electrons and then co-deposited with a rare gas on a 4 K sapphire window. These matrix samples were interrogated in situ either by optical absorption or emission spectroscopy. The results show that species single size up to Ag_5 can be effectively neutralized and imbedded in a rare gas matrix. A new Ag_3 transition based at λ = 305 nm has been found which was not reported before.

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