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Metal-cluster Compounds: Model Systems for Nanosized Metal Particles*

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Meta-cluster compounds can be exploited advantageously to study the evolution, with increasing size of the molecules of the physical properties of metal clusters from molecular to bulk-metal behavior. The metal-cluster molecules are well-defined, stoichiometric, chemical compounds. The molecules consist of a metal core of a variable number of atoms, surrounded by a shell of ligand atoms or molecules. Depending on the compound, the type of metal atom may be varied, whereas the core size can be changed from a few up to several thousands of atoms. Accordingly, these materials provide excellent model systems for monodisperse metal particles, embedded in a dielectric matrix, and can be investigated by the well-known experimental techniques of solid-state physics. © 1998 John Wiley & Sons, Ltd.

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METAL-CLUSTER COMPOUNDS

Polynuclear metal-cluster compounds form an interesting class of systems that, until recently, had been scarcely studied by the physics community.[1, 2] They consist of macromolecules, each macromolecule being composed of a 'core' of a certain number (n) of metal atoms, surrounded by a 'shell' of ligands. The macromolecule can be an ion or a neutral molecule. The important point is that, since we are dealing with chemical compounds, the macromolecules in a given compound are identical. Consequently, the solid formed can be seen as a macroscopically large assembly of identical metal particles, embedded in a dielectric matrix. A major problem with other physical or chemical methods employed so far to obtain metal clusters, e.g. by condensation in atomic beams, by deposition in rare-gas matrices, or in colloids and catalysts, is that one is plagued by a large distribution in particle size. This is a clear drawback if one wants to make a systematic investigation of physical properties as a function of cluster size, since then a variable but homogeneous particle size is an absolute necessity. In the metal-cluster compounds, this goal can thus be realized.

Clearly, the above intuitive conceptual view can only be meaningful for sufficiently large metal cores. Metal cluster compounds with (relatively) small metal cores have been known in chemistry for quite some time, and a decade ago several hundreds of compounds had already been synthesized, with core sizes ranging up to 10–20 atoms, and with a great many different transition-metal elements (iron, cobalt, nickel, molybdenum, ruthenium, rhodium, palladium, silver, osmium, iridium, pla-

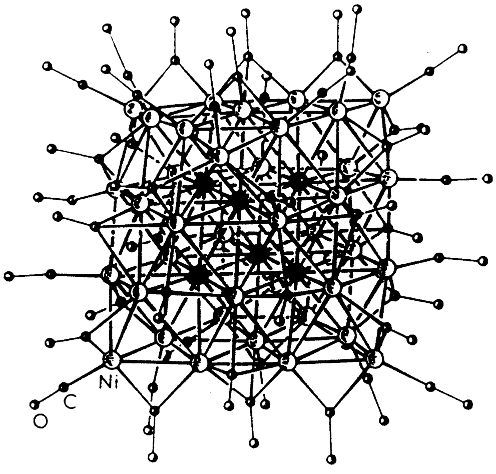

Figure 1 Structure of the metal cluster molecule $[Ni_{38}Pt_6(CO)_{48}H]^{5-}$.

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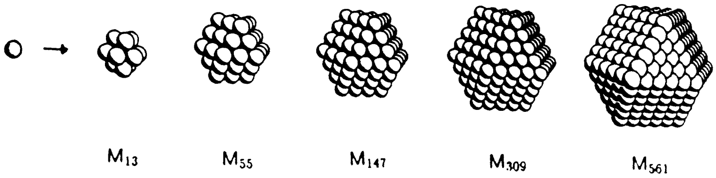

Figure 2 Magic-number clusters M_n, shown for cuboctahedral packing.

tinum, gold etc.). In the last 10 years, however, a few synthetic-chemical groups, notably in Germany, Italy and England, have initiated successful quests to create ever-larger metal cluster molecules, inspired not only by the synthetic challenges involved, but likewise by the growing interest of solid-state physicists in their products.[1–5] For example, within the subgroup of metal carbonyl clusters (metal cores coordinated by CO ligands), very large metal cores, e.g. containing up to 34 Ni atoms or up to 38 Pt or Pd atoms, were synthesized, as well as bimetallic cores consisting of six Pt atoms surrounded by 38 Ni atoms, as in the example shown in Fig. 1. Using phosphine (or related) groups as ligands, neutral cluster macromolecules with large pieces of, for example, Ni_2Se_3 or Cu_2Se as cores have been obtained,[5] such as $[Ni_{34}Se_{22}(PPh_3)_{10}]$, $[Cu_{70}Se_{35}(Pet_3triethylphosphine)_{22}]$ and $[Cu_{146}Se_{73}(PPh_3)_{30}]$. We note that bulk Cu_2Se has semi metallic properties. These materials form molecular crystals; $Cu_{146}Se_{73}$ is the largest cluster compound to date that has been fully characterized by X-ray analysis.

Even much larger clusters, however, have been found in a series of giant metal-cluster molecules, the metal cores of which are members of the series of so-called ‘magic-number’ (full-shell) clusters depicted in Fig. 2.[3] They are obtained by surrounding an atom progressively with additional shells of atoms of its kind. The resulting one-shell, two-shell (etc.) clusters possess the magic numbers of atoms, i.e. 13, 55, 147, 561 and so on. These numbers are the same for icosahedral or cuboctahedral (face-centered cubic) packing of atoms, but the experimental examples mentioned below have cuboctahedral structure. For instance, the two-shell M_{55} core is found in a series of cluster molecules $M_{55}L_{12}Cl_x$, where the metal atom M can be Au, Pt, Ru, Rh or Co. Depending on the metal element, the ligand is for example, PPh_3, PMe_3, $P(t\text{-}Bu)_3$, or $P(p\text{-}tolyl)_3$, and x is 6 or 20. So far, an experimental realization of the three-shell cluster is lacking. However, four-shell and five-shell clusters have been found to be the metal cores in, respectively, Pt_{309}phenanthrioline$_5$*O_{30} and Pd_{561}phenanthrioline$_{36}O_{200}$, and the record to date appears to be the seven- and eight-shell palladium clusters found in $Pd_{1415}Phen_{54}O_{1000}$ and $Pd_{2057}Phen_{78}O_{1600}$. It should be noted that until now no single-crystal samples of these giant cluster compounds could be obtained. The neutral macromolecules form dense but randomly packed solids with only short-range order, as in a glass. In the absence of full X-ray analyses, the precise chemical stoichiometry is evidently uncertain. Notwithstanding, a wealth of direct or indirect physical data are available which appear to agree consistently with the formulations given above, coming from high-resolution electron microscopy, EXAFS, Mössbauer spectroscopy, NMR, calorimetry etc. It should also be realized that, from the three-shell cluster onward, the metal cores in these macromolecules are already large enough to be studied individually by X-ray scattering! The observed reflections confirm the cubic close packing, with metal–metal distances indistinguishable from the corresponding bulk values. In addition to these giant cluster compounds, it has been proven to be possible to synthesize new types of palladium and platinum colloids using the same ligands. These colloids are available for experiments in powder (solid) form, with a very high metal fraction and small size distributions (<10%), and thus nicely complement the metal-cluster molecules. Taken together, the colloids and molecular clusters offer a scale of metal particle sizes ranging from 10 to 100 000 atoms.

The typical size of these clusters (diameters of 1–10 nm) puts them clearly in the class of mesoscopic systems. The metal-cluster molecules may in principle also be exploited to obtain nanocrystalline metals by taking away the ligand shells surrounding the metal cores, e.g. by electrochemical methods. The catalytic properties of the bare and ligated cluster molecules are of great interest, and are being investigated by the chemists with whom we collaborate.

PHYSICAL PROPERTIES OF INTEREST

For physicists these materials form a rich playground by means of which a substantial number of interesting and fundamental physical problems may be studied. We mention the following examples.

Quantum-size effects[6]

For electrons with energies comparable with Fermi energies (E_F) in metals, a nanometer-sized metal cluster is a quantum well, since its De Broglie wavelength is comparable with the cluster size. Thus, the electronic energy-level structure for the metal cluster will be discrete (quantum-size effect), implying that the physical properties will differ from those of the bulk metal, as long as the thermal energy k_BT is smaller than or comparable with the distances δE between energy levels. Furthermore, the statistics of the energy-level distribution in conglomerates of mesoscopic particles is an interesting problem in itself. The relationship to statistical theories for nuclei (random matrix theories: Wigner 1951, Dyson 1962) has been pointed out long ago by Gorkov and Eliashberg,[7] and continues to be a subject of study.[8] Recently, the connection with quantum chaos (nonintegrable systems; quantum billiards) has become apparent,[9] as well as the relation to the t–J Hubbard model and the nonlinear Sigma model.[10]

Size-induced transitions from molecular to bulk-metal behavior

A metal cluster of a few atoms is basically a molecule, with widely spaced electronic energy levels. For the bulk metal, the spectrum is a (quasi) continuum. Clearly, with increasing cluster size, at some point the properties should change from molecular to bulk-like. The question of at what size such a transition will occur has intrigued physicists involved in cluster science, from the very beginnings of this field. As explained below, it depends on the criterion accepted for 'metallic' behavior, and thus on the thermodynamic function considered as well as on the temperature.

Cluster molecules as building blocks for nanostructures

By packing cluster molecules into solids (as is done by chemical synthesis in case of the metal-cluster compounds), one creates a three-dimensional array of quantum wells. Likewise, it should be possible to construct one-dimensional quantum wires and two-dimensional quantum sheets by packing the cluster molecules in the form of a chain or of a monolayer on suitable substrates. By changing the size of the metal clusters, the energy-level structure in the quantum wells may be modified. By varying the size of the ligands which separate the metal cores, the degree of electrical insulation between metal cores may be changed. Such one-, two- or three-dimensional arrays should give rise to novel (and in principle tunable) electronic, optical and electrical properties.

Single-electron tunneling and related effects

In sufficiently small (nanometer-sized) particles, the self-capacitance of each particle, and the capacitance involved with interparticle charge transfer, are so large that charging/single-electron tunneling effects become predominant.[11] Studies with scanning tunneling microscopy (STM) of metal-cluster molecules dispersed on substrates have already been performed by a group in Germany, and by Professor H. van Kempen and co-workers at KUN (Nijmegen). Apart from imaging of the clusters, several other interesting issues are at stake in the tunneling processes between the STM electrodes through a single metal-cluster molecule. The group of van Kempen has observed the single-electron tunneling (SET) effects which are manifested in the I–V curves as regular steps (the 'Coulomb staircase').[12] As argued by them, under suitable conditions one might observe superimposed upon these steps an additional structure due to the discrete energy-level structure (quantum gaps) of a single cluster. Recently, they have claimed to have detected the first evidence for these quantum-size effects. More experiments, however, will certainly be needed to confirm these findings.

REPRESENTATIVE EXPERIMENTS

At Leiden University the physical properties of the metal-cluster compounds have been studied by means of extensive series of pulse-NMR experiments, Mössbauer effect spectroscopy (MES), specific-heat experiments, magnetic measurements, and electrical conductivity and dielectric measurements. In parallel with this work, photoelectron spectroscopy and EXAFS studies are being performed by partners in an EC collaboration. Here only a few important results are mentioned. The majority of the experiments were carried out on the Au_{55}, Pt_{309} and Pd_{561} 'Schmid' clusters (we use this short-hand notation for the full chemical formulae). In addition, the larger Pd_{1415} and Pd_{2057} clusters and the $Pd_{colloid}$ were investigated extensively by specific-heat and magnetic studies. A major reason for investigating these materials is that they are among the largest metal clusters at present available and, in addition, are not air-sensitive.

A most important problem we had to solve was to ascertain the influence of the ligand shell on the properties of the metal atoms of the cluster core. Indeed, the same ligands which are so crucial in keeping the metal cores apart, will at the same time alter the properties of the metal cluster, as compared with those of a bare metal cluster of the same size and symmetry. Fortunately, we have been able to come a long way in answering this problem experimentally. In parallel with these efforts, local density functional (LDF) calculations have been performed by quantum-theorists (N. Rösch, munich G. Pacchioni, Milan) who likewise participate in our EC network on metal clusters research. They have been able to calculate and compare the level structures and magnetic moments of bare *and* ligated nickel clusters, even those as large as up to 44 Ni atoms and with 48 CO ligands![13].

Both the LDF calculations and the experiments agree with the following picture. One may divide the metal atoms of a metal-cluster core into surface metal atoms (to some of which the ligands are bonded) and inner-core metal atoms (in the interior). The metal–ligand interaction is found to be strong indeed, but mainly limited to the surface atoms. The surface atoms of a ligated cluster differ from bulk metal, whereas the inner-core atoms constitute a minute piece of the bulk metal, albeit with strong quantum-size effects in particular for small clusters, evolving towards bulk properties with increasing size. Obviously, the average level separations δE in the electronic spectra of these particles should still be relatively large. By a rule-of-thumb argument, we may estimate δE by dividing the bulk-metal Fermi energy E_F by half the total number of valence electrons in the cluster. For the 3*d* metals in question, there are about 10 valence electrons per atom and E_F is of the order of 5 eV, yielding $\delta E/k_B \simeq 10^2$ K for a particle of 100 metal atoms.

The experimental evidence for the above conclusions was based on a combination of Mössbauer effect spectroscopy (on Au_{55} and Pt_{309}), NMR (on Pt_{309}), specific heat (on all three), and magnetic susceptibility (on the palladium clusters) measurements. The Mössbauer spectra distinguish clearly between surface and inner-core metal atom sites. The isomer shift (IS) and quadrupole splitting (QS) parameters obtained from these MES spectra for the surface sites are very different from the bulk-metal values, being close to literature values for non-conducting metal salts.[14–16] For Au_{55}, the parameters for the 13 inner-core atoms were already close to but not yet equal to the bulk values. Quite recently, we have been able to extend the MES experiments to Pt_{309}. A special trick was needed here, since there is no platinum isotope known that is suitable for MES. By irradiating the Pt_{309} cluster sample with neutrons at the IRI (Delft), a small fraction of the Pt_{309} clusters (1 in 10^6) was transformed into $Pt_{308}Au$, where the Au nucleus could be used as a Mössbauer source (for the absorber, silver foil was taken). The most important result of this study was the finding that the MES parameters for the inner-core sites were undistinguishable from the corresponding values known for the bulk metal.[17] Since the IS parameter is a measure of the 6*s* charge density seen by the Mössbauer nucleus, this leads to the conclusion that, at the inner-core metal sites, the 6*s* charge density is already extremely close to the bulk value. In other words, as regards this particular property, a Pt_{147} cluster core shows bulk-metal behavior.

As mentioned, however, different criteria for 'metallic' behavior can be considered, depending on the physical property of interest. The Mössbauer IS considered depends on the total 6*s* charge density seen by the nucleus (the integrated 6*s* density of states), and will therefore be relatively insensitive to the quantum gaps in the electronic energy-level spectrum induced by the quantum-size effects. On the other hand, physical properties such as the electronic contributions to the specific heat and susceptibility, the NMR Knight shift (K_s) and nuclear spin lattice relaxation time (T_1), do depend on the density of states (DOS) close to E_F. For such quantities, therefore, the criterion for 'metallic' behavior (as juxtaposed to molecular) is obviously the presence of a quasi-continuous DOS close to E_F. Such a quasi-continuum will be reached as soon as the thermal energy k_BT is larger than the level

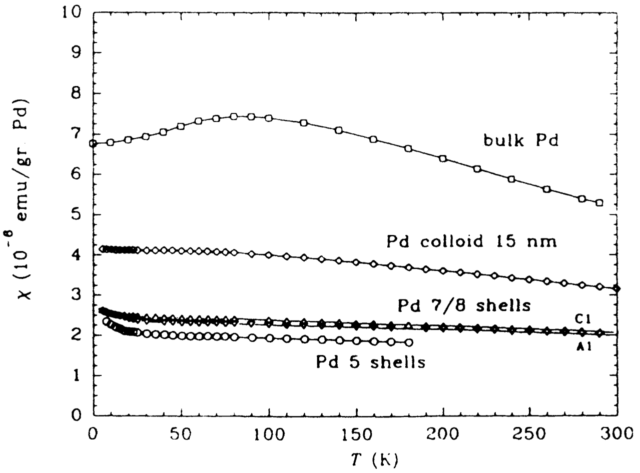

Figure 3 Size evolution of magnetic susceptibility χ of large palladium clusters and colloids towards the bulk behavior.

spacings δE close to E_F. In other words, for sufficiently clusters and/or for sufficiently high temperatures. (It should be noted that level statistics may also produce density fluctuations).

The experimental NMR spectra for the Pt_{309} cluster may indeed be analyzed in terms of a metal-to-nonmetal transition, namely from metallic properties at room temperature and down to about 80 K, to a behavior dominated by quantum gaps.[18] That is to say, the NMR signal at high temperatures showed a considerable Knight shift, and the T_1 followed the temperature dependence given by the Korringa law ($T_1 \propto 1/T$), known to be well obeyed in bulk metals, whereas below about 50 K these metallic properties were lost. Analysis of the observed behavior in terms of quantum-size effects gave satisfactory results, with a value $\delta E/k_B = 30$ K, in reasonable agreement with the rough estimate for E mentioned above.

In contrast to NMR and MES, physical quantities such as the experimental electronic specific heat and susceptibility are not site-specific, being averages over the contributions from all different sites. Nevertheless, these quantities are proportional to the average electronic DOS of the cluster, and therefore should differ markedly from bulk values when, for instance, the surface metal atoms would have a strongly reduced DOS (the fraction of surface atoms is of course quite large in a small particle). Such a strong reduction is predicted by the LDF calculations mentioned above to result from the ligand–metal charge transfer in ligated metal clusters. For the nickel-carbonyl clusters, the reduction of the DOS at E_F induced by the ligand–metal interaction is predicted by the LDF calculations to be accompanied by a complete disappearance of the magnetic moment of the Ni atoms at the surface of the cluster. Since bare nickel clusters are calculated to have magnetic moments per atom comparable with the bulk value (0.6 μ_B/atom), the ligation of a bare cluster should lead to a very strong reduction in the magnetic moment of the cluster as a whole.[13] Indeed, previous magnetic measurements had shown only quite weak magnetic moments, even for very large nickel carbonyl clusters. An extensive magnetic study of a single-crystal sample of a large nickel-carbonyl cluster ($Ni_{38}Pt_6$) was subsequently performed, and confirmed the complete quenching of the magnetic moments of the surface atoms due to the ligands, as predicted by LDF theory.[19]

Other magnetic studies reported have been concerned with a series of platinum and palladium clusters and colloids. In these cases also, evidence for strong reduction for the average DOS at E_F could be obtained. Although bulk palladium and platinum are nonmagnetic, they are strongly Stoner-enhanced paramagnetic metals. In particular for palladium the magnetic susceptibility at low temperatures is quite high. In our experiments we found large, size-dependent reductions of the susceptibility with respect to the bulk, which could be explained in terms of a combination of surface effects and a (size-dependent) reduction of the DOS and thus of the Stoner-enhancement factor;[20] see Fig. 3.

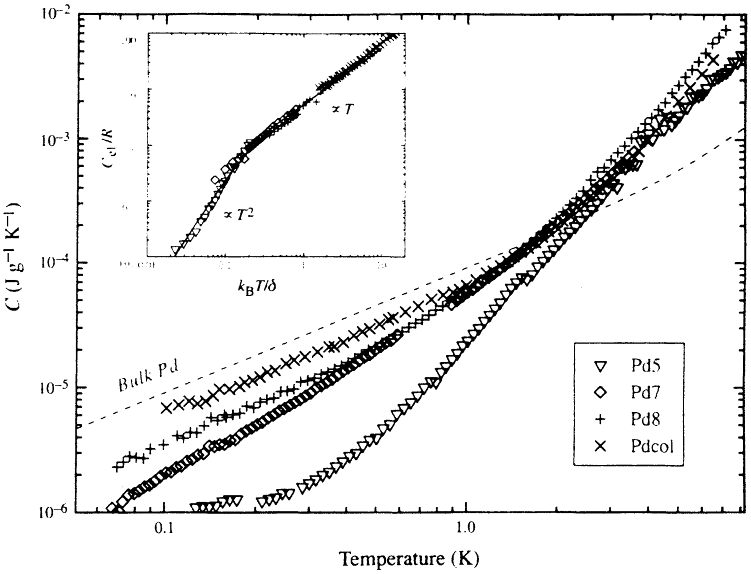

Figure 4 Specific heats of palladium clusters of various sizes compared with bulk palladium. The number of atoms/clusters is 561, 1415, 2057 and 1.25×10^5 for Pd5, Pd7, Pd8 and Pdcol, respectively. The insert shows the electronic contribution (predominant below 1 K) fitted to the QSE theory for the orthogonal distribution. The average level distance δ is 12 K, 4.5 K, 3.0 K and 0.06 K for Pd5, Pd7, Pd8 and Pdcol, respectively. The transition from high-temperature, bulk-like behavior (linear T dependence) to the QSE regime (quadratic T dependence) can be clearly seen in both the theoretical curve (solid line) and the experimental data.

Besides the above classical electrostatic size effects, metal nanoparticles also show prominent quantum-mechanical size effects. Since their sizes are of the same order as the wavelength of the electron in a metal, the energy-level spectrum for the electrons becomes discrete (on a scale of 0.1–10 meV), so that typical metallic properties, based on the pseudo-continuous energy bands characteristic for bulk metals, become lost for thermal energies k_BT lower than the average level spacings . As an example it is shown in Fig. 4 how for $k_BT \leq \delta$ the electronic specific heat of palladium nanoparticles starts to deviate from the linear dependence ($C_{el} \propto T$) that is well known for bulk metals[21]. The solid curve through these data is a prediction for this quantum-size effect based on random matrix theory for the level statistics for collections of metal particles. Even for particles of the same volume, the energy-level structure will still be slightly different for each particle because of the randomness of the interactions of the electrons inside the particle with their environment, for instance with the particle surface (that will always be rough on an atomic length scale). There is a strong parallel with the level schemes of heavy nuclei, the statistical description of which was developed in the 1950s by Wigner and Dyson with the aid of random matrix theory. About 10 years later, this formalism was first applied to metal clusters by Gor'kov and Eliashberg.[7]

Until recently, these effects had not been verified experimentally due to a lack of samples containing clusters of homogeneous size. Lately, however, suitable samples did become available in the form of a series of palladium cluster compounds and colloids, with particle size varying from a few nanometers to 15 nm. The specific-heat results shown in Fig.4 demonstrate a good agreement with calculations based on the random matrix theory, which predicts a T^2 law for the specific heat in the quantum-size region. For more details, see Ref.[21] where the behavior of the magnetic electronic susceptibility is also reported.

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