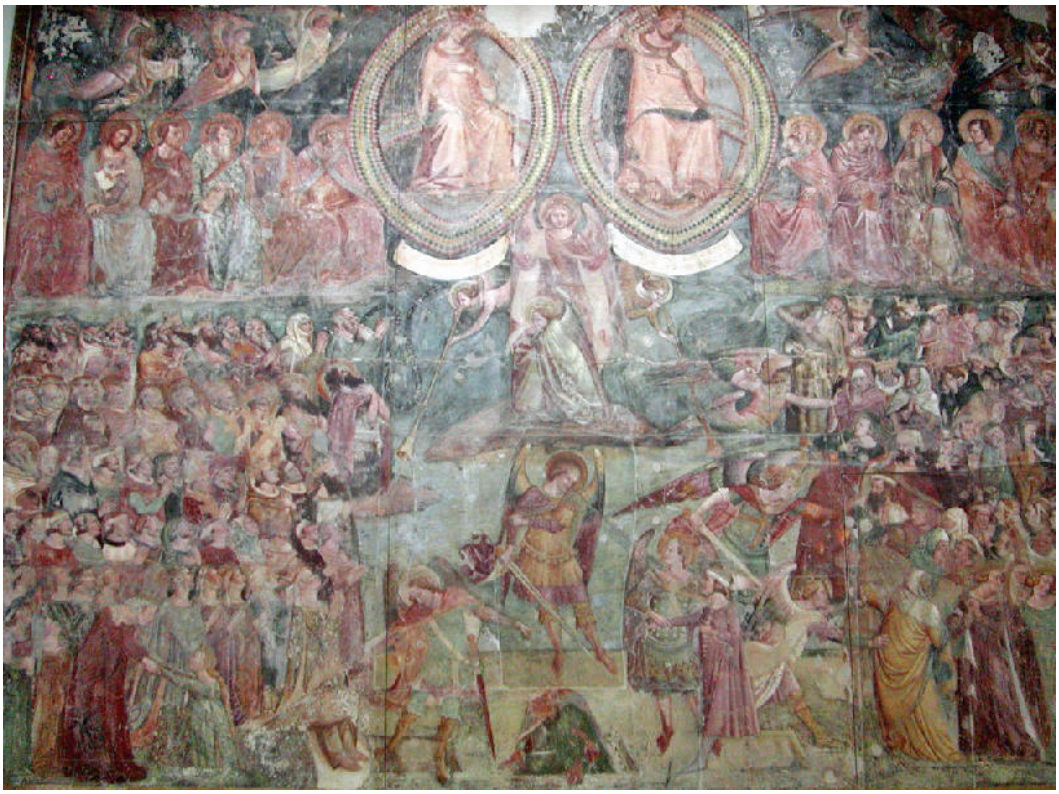
Final Report of the

Workshop on Computational NanoAlloys



Pisa, Italy
21 September - 24 September 2008

Organized by
Alessandro Fortunelli (IPCF-CNR) and Marc Hou (ULB)

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Summary

Metallic nanalloys are of increasing technological importance (with applications ranging from catalysis to electronics and optical and magnetic devices). Computational studies have allowed some understanding of the factors governing their shapes, stabilities, mixing and dynamics. However, significant challenges remain for the computer-aided design of nanoalloy particles and arrays with specific properties. The aim of this Workshop was to explore ways of integrating electronic structure, atomistic and mesoscopic approaches to achieve this goal. The Workshop gathered 27 researchers from Europe, America and the Middle-East in a truly international and friendly environment. A decisive added value was the co-presence of researchers coming from profoundly different backgrounds (chemistry, physics, materials science) but focused on a common topic investigated using different but (after closer examination) concurrent approaches. The Workshop was structured into sessions focused on structural, magnetic, catalytic and optical properties. These sessions were opened by lectures given by selected top-level experimental scientists working in the field, followed by lectures given by theoreticians on related topics. A hands-on and a poster session completed the program.

The Workshop was held at a conference center in Pisa, Italy, and was funded by the Simbioma program of the European Science Foundation and by the Dipartimento Materiali e Dispositivi of the Italian Consiglio Nazionale delle Ricerche.

Scientific content and discussion at the event

The Workshop program and the list of participants can be found below. In the following the main ideas and topics presented in the invited talks will be described. To promote discussion (along lines similar to the tradition of the Faraday Discussions), extended abstracts were submitted in advance by invited speakers and distributed among participants. In keeping with this setting, talks by theoreticians accordingly consisted of 20 minutes presentation plus 20 minutes discussion, talks by experimentalists consisted of 40 minutes presentation plus 10 minutes discussion.

The Workshop was opened by a brief introduction by the convenors, in which the subject of the Workshop was presented: nanoalloys as the meeting point of nanostructures and metal alloys. On the basis of previous experience, it was remarked that the subject of nanoalloys, sharing the same constitutive elements, also shared with nanostructured and alloyed systems the same difficulties posed to theoretical investigation. It was then agreed to distinguish those issues that are intrinsic to nanostructured or alloyed systems from those that are peculiar to the field of nanoalloys, as they derive from the specific combination of the constitutive elements. In fact, it was noted that in the same way that the scope of properties and phenomena is beautifully widened, so are the modeling issues to be overcome when dealing with nanoalloys. Moreover, as an interdisciplinary effort is deemed necessary to solve such issues, attention was requested to the speakers to avoid specific jargon and aim at the maximum possible clarity of language. The desiderable atmosphere of the Workshop was also set, as being extremely informal, friendly and aimed at promoting the highest possible level of scientific discussion in view of reinforcing existing or promoting future collaborations.

The theme of the first session was the structural and mechanical properties of nanoalloys. The Workshop started with a lecture by M. Yacaman, who presented the latest experimental results on aberration corrected electron microscopy, a technique that allows one to study nanoparticles and nanostructures at the highest possible resolution. Aplication of this technique to AuPd and AgAu nanoparticles showed for the first time the feasibility of a direct comparison between theoretical and experimental results. The opening lecture was followed by the presentation by A. Caro, who investigated the link between the phase diagram of bulk alloys and the behavior of nanostructures, focusing in particular on the prediction of the mechanical properties conferred by nanoprecipitates to steel. M. Hou then extended the investigation of the mechanical properties to surfaces and interfaces, with the onset, e.g., of superplastic behavior in cluster assembled materials. M. Mariscal presented results on the kinetics of mixing and shape formation in collision experiments, as well as investigated a novel formalism to predict the control of nanoalloy synthesis via electrochemical deposition. Finally, R. Ferrando illustrated the latest developments in the prediction of epitaxial relationships of nanoalloys supported on model oxide surfaces and the possibility of stabilizing a general class of hcp phases on square-symmetry oxides. The session was ended by short presentations of the posters, that were then posted next to the coffee-break and restaurant areas to allow participants the highest possible level of discussion and scientific exchange.

The discussion at the first session concentrated on the status and perspectives of the theoretical prediction of the structural properties of nanoalloys systems. Recent advances were positively underlined, connected not only with the increase in computer power and accessibility, but also in the development of novel and more accurate and efficient methods, allowing one an unprecedented level of confidence in the exploration of the whole spectrum of sizes, from ultranano to large particles. The connection with experimental results was also analyzed, pointing to further refinements, developments and cross-check in both theory and experiment that still need to be performed in order to finally settle the issue. The importance of having reliable empirical tools with an accuracy comparable to first-principles methods was stressed.

The theme of the second session was the magnetic properties of nanoalloys. The session was started by H. Brune, who presented a detailed experimental study of the correlation between magnetism

and composition in CoFe (and other) islands supported on Pt(111). G. Pastor considered the problem of the prediction of magnetization, magnetic ordering and anisotropy in CoRh nanoparticles via tight-binding methods, as well as universality phenomena and Kondo effects in small $NiCu_N$ (and other) clusters via a combination and comparsion of tight-binding and first-principles approaches. P. Entel introduced the FePt system, illustrated its possible relevance in the field of spintronics, and discussed order/disorder phenomena, magnetism and structural evolution with size of suspended FePt nanoparticles. A. Fortunelli concluded the session by recalling recent developments in the prediction of the epitaxial relationships of supported nanoalloys and tackling the problem of supported magnetic alloys, focusing in particular on the study of CoPt ultra-nanoparticles on MgO(100) via a combination of empirical potential and first-principles approaches and the possibility of generating novel phases with no counterpart in the bulk through a proper choice of the geometrical and chemical features of the support, finally concluding with a preliminary exploration of the influence of the particle/substrate interface on magnetism.

Magnetic properties were also the theme of the fourth session. C. Mottet used global optimization techniques and Monte Carlo simulations in the canonical ensemble to predict the atomic structure and chemical ordering of suspended CoPt particles, concentrating on the crossover among polyicosahedral, decahedral and truncated polyhedra with $L1_0$ ordering and the comparison with available experimental data. D. Spanjaard presented and discussed in depth empirical potentials based on the second-moment approximation and the analytics and foundations of the Hartree-Fock tight-binding model. Representative applications then followed on the FeNi and FePd systems. K. Albe concluded the list of invited talks with an overview of thermodynamic and kinetic effects in FePt suspended particles. He discussed a specific class of (bond-order) potentials together with further simplified Ising-type Hamiltonians, and used them to investigate the structural stability of multiply-twinned particles, the size-dependence of order-disorder transition and the kinetics of ordering in nanoalloys, together with an investigation of the effects of irradiation on the kinetics of attaining equilibrium shape and chemical ordering.

The discussion at the two sessions on magnetic properties highlighted the overall qualitative agreement between first-principles prediction and experimental measurement of magnetism in nanoalloys, but remarked the computational cost of such calculations. This substantial agreement, finally achieved and assessed, opens several interesting possibilities in terms of applications, but also the general problem of deriving more approximate but computationally less intensive approaches that can be used to investigate larger particles or in the systematic exploration of non-collinear magnetic phenomena. Tight-binding methods represent at the moment a convenient choice, but even more simplified techniques should be better investigated to explore the structural behavior of large particles, such as recently proposed Ising-type Hamiltonians and empirical potentials including spin degrees of freedom. After the fourth session, a hands-on session was briefly held, in which participants were allowed to show the capabilities and the results of their software programs, followed by a formal poster session, in which external participants were allowed to present their results and discuss them with invited speakers.

The third session was focused on the relationships between structural and chemical (especially, catalytic) properties. It was open by a lecture by D. Bazin, who illustrated the present status of knowledge of real and model systems in heterogeneous catalysis, recalled the Savarin principle and the volcano curve, set up connections and links to surface science, and concluded by introducing empirical rules to predict the activity of a specific metal(or alloy)/support pair. K. Neyman then introduced the concept of the scalable and non-scalable regimes with respect to structural properties and surface reactivity, and illustrated the effect of alloying with a second metal in PdM (M=Ag, Au, Zn) systems on adsorption and dissociation of small molecules that play a key-role in catalysis. The issue of particle restructuring (both in shape and chemical ordering) after ligand adsorption was also addressed. J. Rossmeils focused on the theoretical modeling and prediction of electro-catalytic activity of metals and alloys in fuel cells, summaryzing the findings of the work by the Norskov's group. He introduced proper quantities that can be conveniently used as descriptors in one and two-

dimensional volcano curves, and illustrated the accuracy, the predictive capability and the agreement with experimental information of such definitions, underlying that this approach was presented specifically for the oxygen-reduction reaction but is in principle of general applicability. He concluded hinting at recent developments in collaboration with M. Mavrikakis's group. R. Johnston presented the results of a thorough investigation on small and medium-sized (N=2-200) AuPd suspended particles. He used advanced and varied global optimization techniques to perform a systematic search of structural families in this composite system, using two different empirical potentials to assess the dependence of the results on the choice of the empirical model and to compare these data with the outcome of first-principles calculations. He raised the issue that none potential so far proposed is able to capture the whole physics of the AuPd system, and encouraged further research on this problem. J. Jellinek presented an analysis of the relationships between homotop energetic ordering within different structural families and relative position of structural funnels with the kinetic behavior and phenomena and the caloric curves in nanoalloys. AlNi small clusters were taken as a prototypical example to illustrate the effect of the cluster size on the composition-dependent trends in the spectra of configurational energies and the peculiar feature of the dynamics of melting, reordering and restructuring.

The discussion at the third session acknowledged the impressive achievements that computational modeling has accomplished in recent years, together with the experimental advances in the in-situ and in-real-time characterization of the formation, evolution and dynamics of reactive species, but also underlined the inherent difficulties presented by this which can be probably considered as the most complex phenomenon (or, probably, ensemble of phenomena) in the field. A number of remaining still unsolved issues were singled out, starting with the general problem of the need of a consistent level of accuracy of first-principles approaches when dealing with such composite and sensitive systems. A coordinated effort was therefore believed to be called for by the nanoalloy (and other) community to make further progress. The lines of possible developments were sketched and the possible actions in this direction outlined.

As M. Broyer was unfortunately unable to attend the meeting and give his contribution on the experimental investigation of the optical properties of nanoalloys because of last-minute severe health problems, the schedule was changed and more space was left for a final general discussion (anticipated in part in the above report). The last session was opened by R. Fournier, who considered highly frustrated AgRb small clusters, in which charge transfer, size and cohesive effects are in strong competition, and that are interesting in view of the search for novel phases and phenomena (such as stable analogues of Zintl compounds). The concept of magic clusters was introduced and electronic and structural magicity was searched for in the given case, together with a detailed structural analysis of empirical and first-principles results. The problem of the choice of proper structural descriptors (or order parameters) was also discussed and solved in an original way. H. Groenbeck introduced a novel class of coated (ligand-protected) pure metal (Au) and nanoalloy systems, to be used a building blocks of nanomaterials in different fields, whose structure was recently solved. He proposed a set of general building principles for such systems, and illustrated its application to several specific examples. Their electronic and spectral properties were analyzed in detail in terms of models invoking electronic magic clusters associated to quantum shell closure. He also discussed preliminary results on the structure and catalytic activity of supported RuSn clusters obtained via decomposition of ligand-protected metal clusters. F. Calvo used advanced Monte Carlo techniques to predict the order-disorder thermodynamic transition in alloy nanoparticles. He considered PdPt clusters with the formation of onion-ring structures at low temperatures and the smooth transition to a solid solution before melting as a function of size (evolution toward bulk behavior). He then contrasted this system with AgPt and AgNi particles, in which partial reordering with increasing temperature or shape transitions to novel types of segregation and demixing were found, respectively. In the AgPt case, possible connections with experimental data on optical (plasmon) response were also discussed. M. Polak concluded the works by discussing the foundation of empirical modeling of the structural properties in nanoalloys and proposing the simplest possible model for describing these effects, based on coordination-dependent bond

energetics. He discussed in detail the connection of this approach with the prediction of surface segregation, and its comparison with experimental data and first-principles methods.

The discussion at the last session and the final discussion recapitulated raised issues, recognized achievements and desiderable future developments, as detailed in the next section.

Assessment of the results and impact of the event on the future direction of the field

The Workshop web site is http://h2.ipcf.cnr.it/alex/WorkshopCNA/workshop.htm.
First of all, it can be remarked that all participants considered the Workshop as being fully successful, as witnessed by the high level of discussion under both the quantitative and qualitative points of view. The fact that many participants had not previously met each other in person witnesses the interdisciplinary character of the Workshop, but above all the fact that the event was important to arise consciousness and stimulate the creation of a community in this field. This was the main aim of the Workshop and the participants agreed that this aim was fully achieved. With this goal in mind, theoretician participants had been requested to send in advance a pdf file with a very schematic but informative description of their previous activity and future perspectives in the field of computational nanoalloys. These documents are posted on the Workshop web site under the heading “Previous work and future perspectives”. This web site will be kept in the future, enriched with contributions from other groups (for example, those who were unable to attend the Workshop because of overlapping previous engagements) that will be invited and welcome, and will constitute the first stone of a database on nanoalloys, to be extended to experimental groups, acting as the basis for future actions in this field. Among these actions, from discussion groups held at the Workshop it was decided to apply in the next future for a CECAM workshop to further strengthen the theoretical community and a COST program to extend this level of involvement to the experimental community working in the field, and commitments were distributed among selected participants to carry out the corresponding initiatives.
From a purely scientific point of view, the focus of the Workshop has been two-fold, and these two aspects have been clearly both distinguished and interlaced from the outset: (i) to monitor and make progress in the general field of metal nanoparticles and nanostructured systems, and (ii) to single out those properties that are unique to nanoalloys, connected with the fact that composition and atomic ordering of the aggregates, in addition to their size, come strongly into play in determining their behaviour. It was observed in the discussion that the intrinsic challenges which the complications due to (ii) pose to computational modeling stimulate the developments of techniques that are also beneficial to (i). A common underlying theme in this respect has consisted in the general issue of building a bridge between quantum and classical world: Deriving classical and semiclassical models and expressions that are based in a self-consistent way on first-principles approaches (as presented in several lectures) has been singled out as a key-point to make decisive progress in the field. As for the intrinsic challenges, (1) due to the permutational degrees of freedom, the number of local minimum configurations is exponentially larger than in the case of single-component systems, and this makes the determination of the most stable structures as a function of size and composition very difficult, even using the most advanced global optimization techniques. Moreover, this permutational freedom translates into the rich variety of novel nanoalloy structures that is continuously being discovered and that start to be understood and catalogued. Several methods have been developed to deal with this problem, among which combined empirical-potential/first-principles approaches appear as the most effective. (2) The finite-temperature properties (temperature-dependent structural transformations, melting, segregation, interdiffusion) of nanoalloy clusters have started to be investigated computationally. However, the corresponding protocols (although fascinating and producing very promising results) are still at a pioneering stage and their efficiency has not been systematically tested and assessed. More work is deemed necessary, particularly in the distinction of thermodynamic and kinetic effects in order/disorder transition. Plans to carry out such a work have arosen from the discussion. (3) The growth of both isolated and supported nanoalloy clusters as well as cluster-assembled films has been investigated in very few cases, and on time scales of up to microseconds, with only exploratory use of accelerated molecular dynamics or kinetic Monte Carlo methods to sample long-time behaviour or of object kinetic Monte Carlo simulations and informed continuum or quasi-continuum methods for a coarse description of larger length scales. This topic has been recognized as probably the one at a most rudimental stage, and in need of further studies and collaborations. (4) The status of the properties of gas-phase, supported or coated nanoalloy clusters (including their chemical reactivity) has been subject to particular attention, and has been found to be promising, especially as far as

magnetic and optical properties are concened. The main issues still concern catalytic properties: systematic computational studies on the interaction with adsorbed molecules (reactants, passivating agents, surfactants), are needed to shed light and provide information essential to rationalize experimental data. Overall, it has emerged from the discussion an optimistic attitude, as in several subjects structure-property relationships are becoming accessible to theoretical and computational investigation, and the optimization and the determination of the most interesting properties of nanoalloy is evolving from the empirical method of trial and error to a more informed and advanced stage. A computer-aided design of nanoalloys thus seems to be foreseeable in the next future. It is worth noting that the most notable results have been obtained or appear to be obtainable in a near future via interdisciplinary work and collaborations, confirming the aim of the Workshop to stress the need of an integration of the most advanced theoretical/computational techniques and expertise in materials modeling, and therefore of a coordinated effort of several research groups on an international scale. This justifies the original intent of the Workshop to provide an overview of the field of computational treatment of nanoalloys by bringing together experts covering all relevant theoretical/computational techniques, with the aim of (1) creating a common language and protocols among groups working on particles in various environments, (2) assessing the feasibility and accuracy of integrated first-principles/empirical-potential and microscopic/mesoscopic computational tools for the description of nanoalloys (electronic structure and atomistic up to mesoscopic methods).

To conclude, it is noteworthy, but fully in line with the spirit of the Workshop, that a few issues, such as the problem of modeling of AuPd particles with an empirical potential or with coordination-dependent models, have stimulated immediate collaborations among the participants, that have already brough about possible solutions to the problems raised in the discussion.

International Workshop on Computational NanoAlloys

21 September - 24 September 2008

Program

21 September Sunday

18:00-23:00 **Reception and registration**

20:30 Dinner

Note: Talks by theoreticians consisted of 20 minutes presentation and 20 minutes discussion. To promote discussion, extended abstracts have been submitted in advance and distributed to invited speakers.

22 September Monday

9:00-9:05 **Opening**

9:05-9:55 Miguel J. Yacaman
Study of bimetallic nanoparticles using Aberration Corrected Electron Microscopy

9:55-10:35 Alfredo Caro
The computational modeling of alloys: from ab initio and thermodynamics to nanostructures

10:35-11:15 Marc Hou
Surface and interface phenomena in nanoalloys

11:15-11:40 Coffee Break

11:40-12:20 Marcelo Mario Mariscal
Generation and properties of bimetallic nanoparticles

12:20-13:00 Riccardo Ferrando
Epitaxy of Supported Nanoalloys: PdPt/CaO(100)

13:00-13:20 Poster presentations

13:20-15:00 Lunch Break

15:00-15:50 Harald Brune
Atomic Scale Correlation of Magnetism and Composition in Bi-Metallic Nanostructures

15:50-16:30 Gustavo M. Pastor
Magnetic impurities in nonmagnetic metal clusters: A survey of the Kondo physics in the limit of ultimate confinement

16:30-17:00 Coffee Break

17:00-17:40 Peter Entel
Ab initio simulations of multimetallic transition metal clusters

17:40-18:20 Alessandro Fortunelli
Epitaxy of Supported Nanoalloys: CoPt/MgO(100)

20:30 Dinner

23 September Tuesday

9:00-9:50 Dominique Bazin
Bridging Nanoscience and Surface Science to Understand Heterogeneous Catalysis

9:50-10:30 Konstantin Neyman
Density-Functional Studies of Bimetallic Nanostructures Relevant to Catalysis and Beyond

10:30-11:10 Jan Rossmeils
Electro-catalytic activity of alloys - studied with DFT

11:10-11:40 Coffee Break

11:40-12:20 Roy Luigi Johnston
Theoretical Studies of Palladium-Gold Nanoclusters

12:20-13:00 Julius Jellinek
Nickel/Aluminum Clusters: Analysis of Composition- and Size-Evolution of Structural Characteristics and Dynamical Peculiarities

13:00-15:00 Lunch Break

15:00-15:40 Christine Mottet
Order-disorder Phase Transition in CoPt Nanoparticles

15:40-16:20 Daniel Spanjaard
Influence of Chemical Order on the Magnetic Properties

16:20-17:00 Karsten Albe
Atomic Scale Computer Simulations of FePt Nanoparticles: Thermodynamics, Kinetics and Irradiation Effects

17:00-17:30 Coffee Break

17:30-19:00 Hands-on and Poster Session

20:30 Dinner

24 September Wednesday

9:00-9:50 Michel Broyer (cancelled for severe health reasons)
Linear and non linear optical properties of nanoalloys and core-shell bimetallic clusters

9:00-9:40 Renè Fournier
Structural Order in Bimetallic Ag_nRb_n Clusters (n=2-10)

9:40-10:20 Henrik Groenbeck
Structural and electronic properties of ligand protected, bare and supported RuSn and Au clusters

10:20-10:50 Coffee Break

10:50-11:30 Florent Calvo
Segregation, core alloying, and shape transitions in bimetallic nanoclusters

11:30-12:10 Micha Polak
Distinct Effects of Coordination-Dependent Bond Energies on Surface Segregation in Alloy Nanoclusters: Modeling Based on DFT surface-energy data

12:10-13:00 **Final Discussion and Perspectives**

13:00-15:00 Lunch Break
15:00 Departure

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