

## Recent Investigations of Size and Interface Effects in Nanoparticle Composites

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With 4 Figures

### *Abstract*

Nanoparticles, small in all three dimensions, exhibit pronounced size and surface effects. There are broad fields of technical applications for nanoparticle-based composite materials taking advantage of these effects. An essential drawback is that such systems require stabilization, causing the free and clean particle surfaces to be transformed into very complex interface regions.

After a general introduction, four experiments are presented which shed some light upon different aspects of these complex interfaces. They were performed by using 2 nm Ag nanoparticles and applying optical Mie plasmon spectroscopy. The unique feature of these experiments is that spectroscopy was performed with the free particles in a cluster beam and after depositing and embedding them, and, hence, quantitative comparisons could be performed.

### *Zusammenfassung*

Ausgeprägte Nanostrukturierungseffekte finden wir in Nanopartikeln, da diese in 3 Dimensionen klein sind. In Vielteilchen-Systemen/Kompositen werden sie vielfach für technische Anwendungen eingesetzt, welche die auftretenden Partikelgrößen- und Oberflächeneffekte ausnützen. Grundlegender Nachteil vieler solcher Systeme ist, daß sie durch ein Wirtsmedium stabilisiert werden müssen. Dadurch werden die freien, sauberen Teilchenoberflächen in komplexe Grenzflächenbereiche überführt.

Nach einer allgemeinen Einführung werden vier Experimente vorgestellt, die unterschiedlichen Aspekten dieser Grenzflächen gewidmet sind. Sie wurden alle mit 2 nm großen Ag-Teilchen durchgeführt, und es wurden Mie-Resonanzen als empfindliche optische Sensoren für elektronische Eigenschaften untersucht. Die Experimente sind dadurch ausgezeichnet, daß sowohl an den freien Teilchen im Strahl als auch nach Deposition und nach Einbettung spektroskopiert wurde, so daß Unterschiede quantitativ ermittelt werden konnten.

### **1. Introduction**

The unique properties of nanostructured materials, and in special, of nanoparticles (KREIBIG and VOLLMER 1995), most commonly are interpreted as size-effects, i.e.  $N$ -effects, where  $N$  is the number of atoms per structural unit.

These effects are extremely interesting for basic research, since we can observe the “birth” of the solid state by varying  $N$ .

There is a second class of nano-effects, which is due to the surface of the structural units. Nanostructurization means, thus, both, breaking of crystal symmetry, and creation of new surfaces and/or interfaces. Surface of a particle can, however, only be clearly defined and distin-

guished from an inner volume, if  $N > 50$ . This may be introduced as a limit to distinguish between *molecular* and *solid state* clusters.

The nano-effects due to surface are theoretically much less understood, notwithstanding the intense investigations, e.g. in the field of heterogeneous catalysis, or in the succession of the pioneering work of GLEITER'S group with nanocrystalline, grainboundary-rich materials.

We have to distinguish between *surfaces* of the free, uncontaminated particles and *interfaces* covered by foreign dielectric, semiconducting, metallic or superconducting materials, liquids or solids, adsorbates, substrates, embedding media etc. Interfaces are much more complex, consisting, both, of particle surface and foreign material surrounding parts of, or the whole, particle. To give only one example: in special cases of insulating or semiconducting matrix, Schottky barriers emerge.

Surfaces and interfaces include storage of large amounts of surface/interface energy, and this renders many kinds of nanoparticles, in particular the metallic ones, to be energetically instable, one of the worst drawbacks of nanotechnology.

These energies lead to a dramatic struggle between surface and inner volume. Both try to obtain their respective stable energy minima which require controversial particle structures. While for the surface this structure is something close to a spherical shape, it is for the inner volume the crystal structure of the bulk. During particle growth, first the surface is dominating, while towards large particles, the volume is the winner.

To give an example: Using the bulk value of the specific surface energy of silver, this surface energy for the simple case of one spherical silver particle, 10 nm in diameter, yields about 5 keV. In  $1 \text{ mm}^3$  of a many-particle system with a filling factor of  $10^{-4}$  the energy of about 10 mJ is stored in the particle surfaces.

The classical Surface Sciences, dealing preferentially with well-defined crystal planes, cannot, however, be very helpful to treat these surfaces/interfaces in a realistic manner, since they consist, beside some flat facets, mainly of irregular structures, edges and corners with low coordination numbers, all with different electron energy states.

The practical situation is even worse, if, as usual for technically applied many-particle composites, these particles are statistically varying in size, shape, interior structure, next-neighbor interactions, etc.

As a consequence of the additional energies, most inorganic nanostructured systems in nature and technology have to be stabilized, either by passivating them with stabilizing coatings, or by depositing them onto some rigid substrate or by embedding them in some host material.

In general, the model of a free nanoparticle is, therefore, not relevant, even approximatively. Instead, the more complex building units are particles plus the special surroundings, i.e. particles "dressed" by interfaces.

As an example, the famous Gold-55-clusters (SCHMID 1993), in fact are "dressed" metal-organic compound clusters, consisting of a metallic core and the surrounding and stabilizing triphenylphosphine shell plus additional bound chlorine ions as structural units.

Despite intense research, our knowledge about these *realistic* interfaces between particles and chemically variable surrounding materials is rather poor, especially because of their immense variability. In most cases, the electronic interface states or "adsorbate" states are unknown, both experimentally and theoretically.

In fact, their knowledge would be very important, not only for existing technological applications like the heterogeneous catalysis, but also for novel technologies like the expected break-through towards true small-scale nanostructurization in digital electronics or the "func-

tionalization” of nanoparticles by directed adsorption of organic or bio molecules in order to use them as selective antibody tracers for special molecules like e.g. special cell-proteins.

For sure, these interfaces are one of the essential challenges for future research in nanoscience. And nanoparticles appear to be the best suited model-systems for this purpose. In particular, embedding them in absorbing semiconductor and metal matrices, (i.e. semiconductor doping with clusters) may open interesting new applications.

In what follows, we present four experimental investigations which shed some light onto different nanoparticle interface properties.

## **2. Mie Resonances as a Sensor Tool for Interface Investigations**

One of the most pronounced nanoparticle effects is the optical excitation of *Mie resonances* in metallic particles (KREIBIG and VOLLMER 1995). These surface plasmon polaritons are caused by restoring forces which are due to electric surface charging by an external optical field. Hence, they are nano-surface effects, and any changes at the surface, e.g. the transformation of the surface into an interface by covering the surface with some host material, strongly influence these resonances.

Starting 35 years ago (KREIBIG and VON FRAGSTEIN 1969), we still use the Mie resonances as highly sensitive tools for nanoparticle interface investigations, e.g. physical and chemical reactions at the particle surfaces. By the way, this is not a novel idea: in the beginning of the 20<sup>th</sup> century, R. ZSIGMONDY introduced the Mie resonances to chemical analysis. He received the first Nobel Prize in the field of nanoscience, at that time called “colloid science”, in 1925 for his pioneering work with gold nanoparticles.

Conventional optical spectroscopy requires macroscopic samples of many particles, i.e. nanoparticle based nanocomposites. Only recently, single particle extinction spectroscopy was successful (SOENNICHSEN et al. 2000).

For practical reasons we selected silver as particle material, since these particles are world champions in strength and spectral selectivity of Mie resonances.

Any quantitative investigation requires comparison with a proper reference. In our case, this is the *same* Ag nanoparticle but with *free*, uncontaminated surfaces. This appears to be the only confidential reference.

For this purpose, we produce a beam of free Ag nanoparticles in vacuum by a thermal, high efficiency source THECLA (HÖVEL et al. 1993), the particles of which are then, both, deposited onto solid substrates and, by co-deposition, embedded in matrix. In our long-term investigation project, the surrounding materials are systematically varied. Mean particle sizes can be varied between 250 and 2000 atoms/particle, i.e. 2 and 4 nm diameter. Such particles combine (almost) developed bulk electronic band structure with extremely large surface. The unique feature of the experiments is that spectroscopy is performed with the free particles as well as after depositing and embedding them, thus enabling, for the first time, quantitative analysis of the differences between free surface and different kinds of interfaces.

The Mie extinction spectra of Ag nanoparticles resemble Lorentz bands and they have, at least, three features indicative for surface and interface properties: > the band width, > the spectral band position, > the additional background extinction by the optical 4d-5sp interband transition edge. Figure 1 shows the extinction spectra of Ag nanoparticles in the free beam and after deposition on, and after embedding in, glassy SiO<sub>2</sub>.

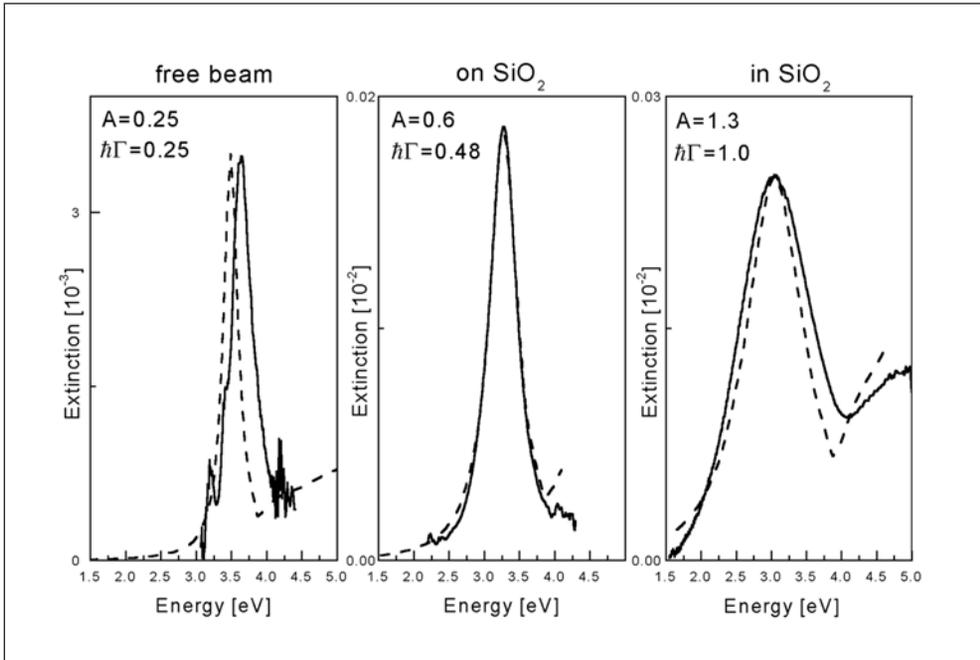


Fig. 1 Measured optical absorption spectra of Ag nanoparticles ( $2R = 2 \text{ nm}$ ) and comparison with calculated spectra. *Left*: free particles in the beam. *Center*: Same particles, deposited upon  $\text{SiO}_2$ -glass substrate. *Right*: Same particles, embedded in  $\text{SiO}_2$ -glass. Calculations (dashed lines): Mie theory with literature data (JOHNSON and CHRISTY 1972) and  $A$ -parameter corrections.  $\hbar \Gamma$  in [eV].

Spectroscopy of composites, yielding averages over many particles, requires well defined, uniform systems to enable quantitative statements about single particles. In our samples, size distributions were determined by TEM and involved in the evaluations. In all investigated samples, the particle distances were sufficiently large to prevent neighbor-interactions. Most problematic are inhomogeneities in the substrates and embedding media, causing different interfaces for different particles. If their characteristic lengths are of the order or larger than the particle sizes, their influences will increase with decreasing size due to reduced averaging out. These effects are very general, contributing e.g. to additional broadening of the overall-spectra. They are, of course, absent exclusively in the free particle beam. As an example, in  $\text{SiO}_2$  matrix we found an upper limit of 20 % of the bandwidth for this “inhomogeneous” broadening of the Mie resonances.

In the following we present results of four experiments on different substrates and embedding hosts, each to demonstrate one particular interface effect.

### 2.1 First Experiment: Silver Nanos Embedded in Fullerite: The Static Charge Transfer

Our sensor Ag nanoparticles were embedded in Fullerite, i.e. solid  $\text{C}_{60}$  material, by co-deposition (GARTZ et al. 1999). Their optical absorption spectrum, obtained by subtracting the spectrum of pure fullerite, proved to be broadened and red-shifted compared to the spectrum of

the free particles in Figure 1 (left). As a second reference, we calculated the extinction spectra from MIE's theory.

The observed peak shift is explained by two superimposing effects: First, the Maxwell boundary conditions of the particle surface are changed by the dielectric function of the embedding host material, giving rise to strong "dielectric" shift (which is already included in the spectra calculated from MIE's theory).

Second, non-classical static charging of the Ag particles occurs leading to an additional shift  $\Delta\hbar\omega$ . Its numerical value is plotted in Figure 2. The underlying model is as follows (HÖVEL et al. 1993, KREIBIG et al. 1998):

- (i) The whole particle/matrix-system arranges itself such that there is equilibrium of the chemical potential (or Fermi-energy  $E_F$ ) in the whole sample. This requires charge transfer from the particles into the Fullerite, and the equilibrium is established by thus generated additional Coulomb energy. Since the particles are isolated in the matrix, the conduction-electron density  $\rho$  in the particle is thereby changed. Such *static charge effect* is expected to occur generally in nano-composite systems.
- (ii) The resonance frequency of the conduction-electron plasma in the Ag-particle depends on the electron density  $\rho$ . The change of  $\rho$  by static charge transfer, thus, causes an additional spectral shift of the Mie resonance.

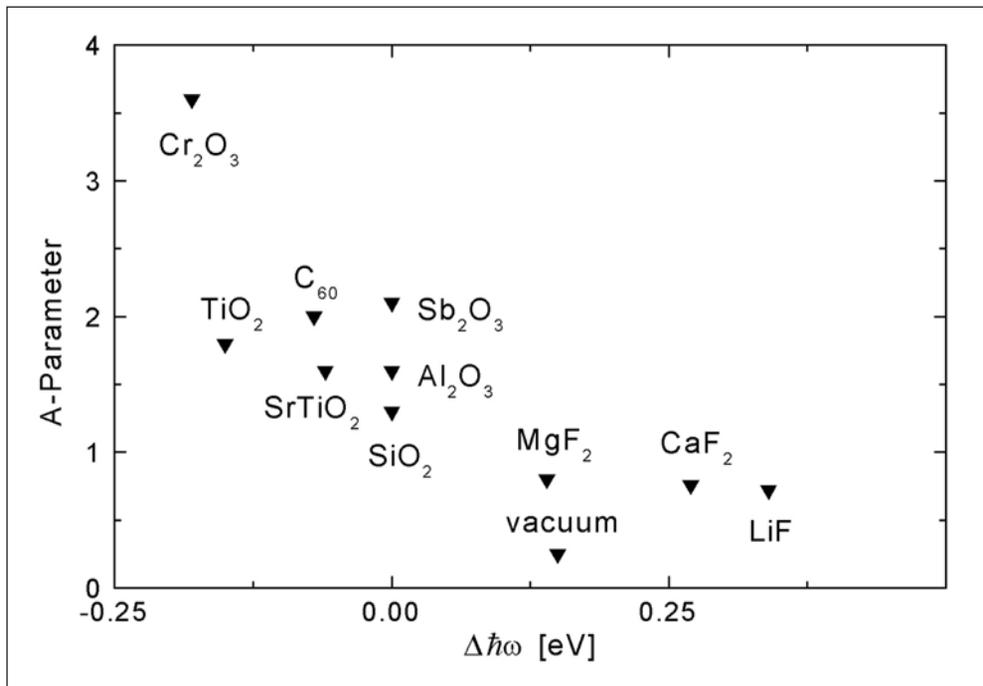


Fig. 2 Summary of experimental results for interface charging effects between Ag nanoparticles and various embedding media: Peak shift  $\Delta\hbar\omega$  (static charge transfer) versus broadening parameter A (dynamic charge transfer). Due to quantum size effects, A of vacuum amounts to 0.25. Systematic differences of the magnitudes of these effects occur between oxides and fluorides.  $\Delta\hbar\omega \neq 0$  for free particles ("vacuum") since the zero was calibrated to Mie calculations using the optical parameters of JOHNSON and CHRISTY (1972).

Numerical evaluation of this model yielded the clear result, that each  $C_{60}$  which is in *direct* contact with the Ag nanoparticle surface in the composite, pulls *one* conduction-electron out of the Ag particle which is then located in one of the electronic interface states. In the present case, the particles loose, thus, about 20 % of their (delocalized) conduction electrons with consequences upon Fermi energy, lattice constants, band structure etc. However, charges are not really removed, but an electric double layer is formed in the interface region.

Hence, the particle material might no longer be called “silver”; instead the interface effects have created a novel metal.

## 2.2 Second Experiment: Interface Damping of Mie Resonances

Again, Ag clusters ( $N \approx 250$  atoms) were produced by THECLA and their optical extinction was measured in the three different states of the free cluster beam, the clusters deposited on a solid substrate and the clusters embedded in matrix of the same material. The special feature of this series of experiments was that a wide range of different host materials was investigated.

Drastic differences of the respective Mie resonance spectra were found for most of the different substrate/host materials (HILGER 2001) which are not included in the classical Mie theory. One example with glassy  $SiO_2$  as surrounding medium was shown above in Figure 1.

The resulting peak shifts were already discussed in 2.1. Now we concentrate upon the apparent band broadening. These effects essentially remain, even if we reduce them for the above discussed inhomogeneous broadening effects. For interpretation, the following model of *dynamic interface damping* was introduced (HÖVEL et al. 1993 and KREIBIG et al. 1998):

- (i) We assume the formation of chemisorption interface states yielding broad energy bands due to interactions with topologically different surface atoms. There are two possible situations: first, these bands are close above  $E_F$  of the Ag particles and can be temporarily occupied by tunneling cluster electrons, second, their energies are far above  $E_F$  and no such transitions are possible. In the first case, charge fluctuations take place in the interface region.
- (ii) These fluctuations may be monitored, if a Mie plasmon resonance is excited. Then, part of the impulse of the collective plasma excitation is lost by each electron transition into an interface state and back to the particle. Hence the common phase of the collective motion of the electron plasma is reduced, leading to increased *phase relaxation* of the plasma resonance, and, hence to broadening of the Mie absorption band. In this model, the broadening is characterized by the *interface parameter*  $A$  depending on the fluctuation strength and, hence, on the details of the electronic interface states. Formally,  $A$  is introduced *via* a reduced relaxation time  $\tau$  of the free Drude electrons in the cluster due to surface/interface interactions:  $\tau_{\text{particle}} = \tau_{\text{bulk}} + A v_F/R$  with  $v_F$  the Fermi velocity and  $R$  the particle radius.  $A$  is evolved from the measured extinction spectra by inverting MIE’S theory (KREIBIG and VOLLMER 1995).

The different numbers and kinds of interface states for deposited and for embedded clusters explain why the latter exhibit larger broadening, by far (see Fig. 1). For deposited particles, surface tension and possible plastic deformations of the clusters and the underlying substrate determine the relation between the relative amounts of free surface and interface and, hence,

the magnitude of interface effects, while embedded clusters exclusively exhibit interfaces (HILGER et al. 2001). In a recent publication, this model has been treated (PINCHUK and KREIBIG 2003).

Figure 2 shows a compilation of measured  $A$ -parameters *versus* charge transfer peak shift  $\Delta h\omega$  for different host materials.

A final comment may be added here: as leading order approximations the models of 2.1 and of 2.2 are treated here independently. In fact, part of both effects is interconnected by Kramers-Kronig relations. Efforts to find a common description by introducing some complex interface parameter are in work.

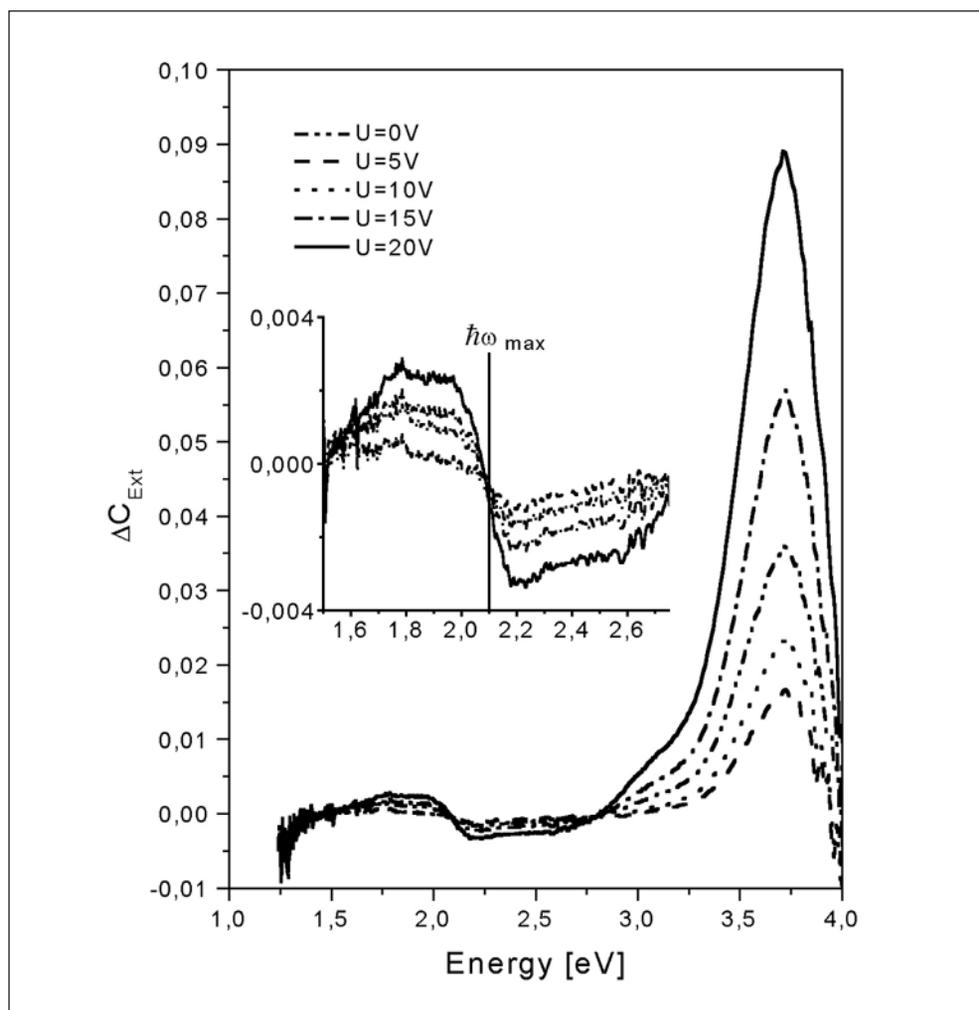


Fig. 3 Ag nanoparticles embedded in ferroelectric PZT: Measured absorption changes  $\Delta C_{\text{ext}}$  due to varying bias voltage. The large contribution at 3.7 eV is due to the PZT interband edge and also present in the particle-free PZT. (Prior to the experiment,  $-20\text{V}$  had been applied, and thus, first the remaining hysteresis-effect had to be rebuilt, before the positive voltage caused the increase of the absorption). The small contribution at  $h\omega_{\text{max}}=2.1\text{ eV}$  is due to the changes of the Mie resonance of the Ag particles. This effect is magnified in the inset.

### 2.3 Third Experiment: Ferroelectric Surroundings

An interesting question arises, to which extent the particular charging effects in the interface region may be artificially varied and what are their effects onto the Mie resonances (VON HOFE 2001). We chose ferroelectric PZT (lead-zirconate-titanate) as an embedding matrix<sup>1</sup>. Two films were deposited on a quartz substrate by help of spin coating, and in between a low coverage monolayer of Ag particles was included. The experiments were first only performed at room temperature. DC voltages were applied between a top ITO and a bottom gold electrode and the according Mie resonance spectra were recorded. The same films, but without Ag particles acted (beside the free clusters) as additional reference. First, the ferroelectric behavior of the films was confirmed by measuring their polarization hysteresis loops which proved to be well developed. Next, optical transmission spectra were measured with increasing external bias from  $-20$  to  $+20$  V dc. The resulting electrostatic fields are up to  $2.5 \cdot 10^8$  V/m. The field direction was parallel to the Poynting vector; we did not yet search for effects in polarized light. The samples exhibited a static conductivity of  $\approx 10^6 \Omega \text{ m}$ . A sharp Mie resonance occurred at  $2.07$  eV with a width of about  $0.7$  eV and shifted against calculated zero-field spectra by as much as  $-0.6$  eV. This shift indicates a strong static charge transfer from the Ag particles into the interface region.

By increasing the bias voltage, two effects in different spectral regions occurred. In Figure 3 only the field dependent *differences* between the extinction spectra with and without field are shown.

The stronger effect is a field dependent increase of extinction at the edge of the fundamental absorption of the PZT itself around a fixed energy of  $3.7$  eV. It exhibits a clear hysteresis behavior and occurs also in the particle free reference sample.

More interesting for our purposes is the bias-effect in the spectral region of the Mie resonance. As also shown in Figure 3, there is a slight extinction change  $\Delta C_{ext}$  in the particle-containing sample which is clearly enhanced with increasing bias voltage. The shape of the difference spectra indicates a red shift of the Mie peak with increasing electrostatic bias field. Also this effect exhibits clear hysteresis effect.

A careful Kramers-Kronig evaluation yielded the result that about one third of the observed Mie peak shift is due to the changes of the PZT-refractive index induced by the extra field dependent absorption at  $3.7$  eV (see Fig. 3). Two thirds remain to extra particle and interface effects of unknown origin. Among them might be bias-induced non-linearity of the plasmon excitation, bias induced extra static charge transfer, etc. The interpretation of these results is in work.

### 2.4 Fourth Experiment: Band Structure Effects

Up to now, all observed and described nano-effects are due to the  $5$  sp electron (conduction electron) plasma in the Ag particles. We demonstrate now, that additional size/interface effects occur with the  $4d$  electron excitations.

In bulk Ag, the low energy optical interband transition edge at about  $3.8$  eV is due to  $4d \rightarrow 5sp$  electron-hole transitions. Usually this is described in terms of the complex interband susceptibility

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$$\chi^{\text{interband}}(h\omega) = \chi_1^{\text{interband}}(h\omega) + i \chi_2^{\text{interband}}(h\omega). \quad [1]$$

These excitations appear as background in our Mie resonance extinction spectra. They were numerically separated from the Mie extinction in the measured spectra by a careful Kramers-Kronig analysis (HILGER 2001).

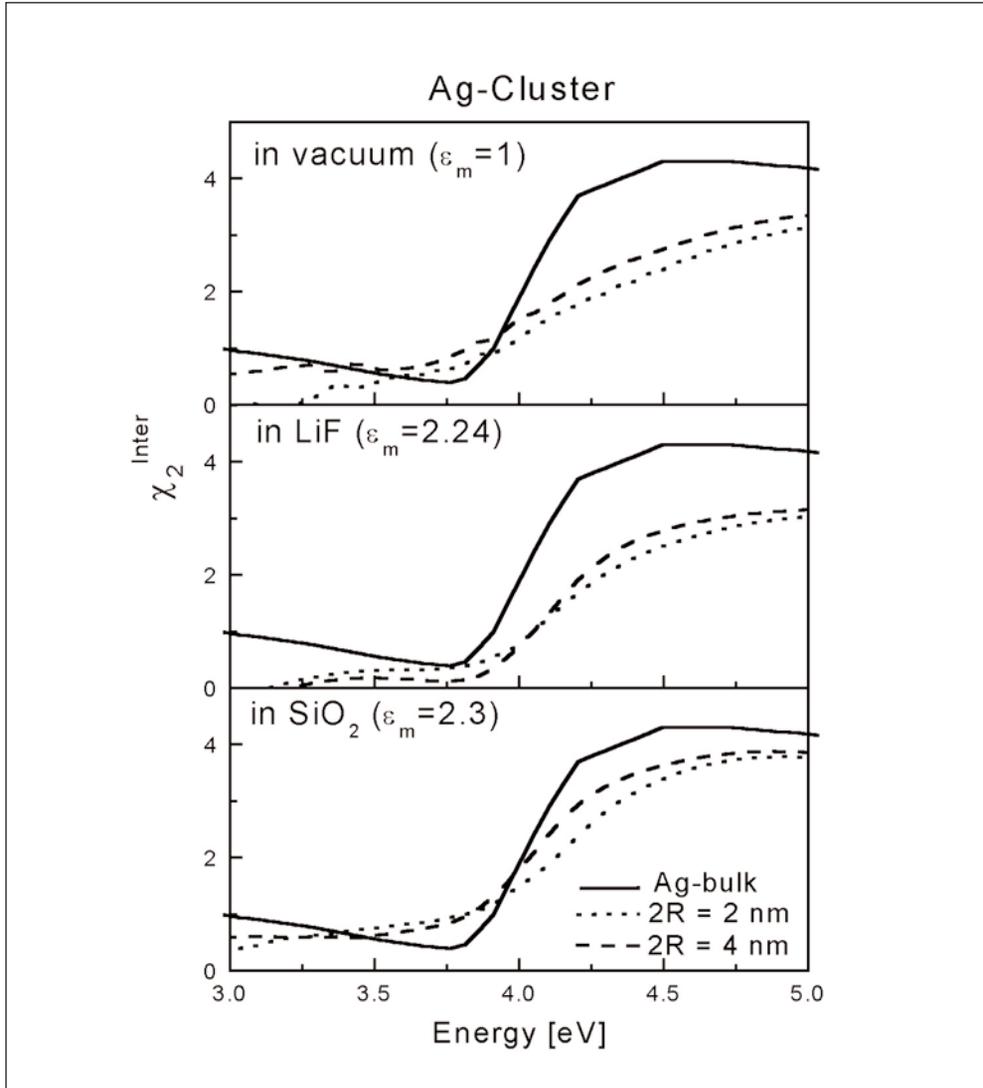


Fig. 4 Development of electronic bandstructure in Ag nanoparticles embedded in different matrix media. The low frequency 4d–5sp interband transition edge is expressed by the imaginary part of the complex electric susceptibility  $\chi_2^{\text{interband}}(h\omega) = \text{Im}\{\chi^{\text{interband}}(h\omega)\}$ . Shown are the band edges for  $2R = 2$  nm and 4 nm particles, as evaluated from experiments on Ag nanos in the free beam (vacuum), and embedded in LiF and  $\text{SiO}_2$ , respectively. For comparison, the edge of bulk Ag is plotted as obtained from proper evaluation of literature data of (HAGEMANN et al. 1974).  $\epsilon_m$  is the dielectric function of the respective embedding medium.

By changing the seeding gas of the cluster source from Ar to Xe the mean particle size  $2R$  could be varied from 2 nm ( $\approx 250$  atoms) to 4 nm ( $\approx 2000$  atoms). In Figure 4 the spectra of  $\chi_2^{\text{interband}}(h\omega)$  of our particles are compared with calculated bulk values. Results from three different surroundings are shown: vacuum, LiF and SiO<sub>2</sub>. There are two important features:

- (i) In the *free* Ag particles, these transitions prove to differ strongly from the bulk. Clearly, the interband transition edge is smeared out and its onset is red-shifted and this the more, the smaller the particles are. This was already detected earlier in *embedded* Au-clusters (KREIBIG 1978). It clearly indicates that the electron interband structure is not yet fully developed in 2 nm and in 4 nm metal particles. The deviations are clearly larger for the smaller particles, yet it appears open whether the leading effect is to be attributed to size or to surface effects. The first would be expected from the fact that the k-vector of Bloch waves is no longer well defined in strongly confined electron systems. The second may be due to the fact that essential part of the particle atoms is forming the surface.
- (ii) A surprising additional, novel effect was discovered when evaluating analogously the experimental spectra of the same particles *embedded* in different host materials. As also shown in Figure 4, embedding in LiF and SiO<sub>2</sub>, respectively, yielded a clearly better approach to the bulk spectra, i.e. a reduction of the interband nano-effect.

As a consequence of these findings, the development of the band structure is obviously supported by the existence of (dielectric) embedding media. These media probably reduce, *via* the formation of the complex interface region, the potential step at the particle surface.

Again, the role of the electronic interface states is an open problem. From Figure 2 we see that the dynamic and static interface effects are large in the case of oxides like SiO<sub>2</sub> but smaller in fluorides like LiF. In correspondence, the interface influence onto the particle band structure is larger in SiO<sub>2</sub> than in LiF. For closer understanding, it appears that band structure calculations including the existence of interfaces are required.

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