3 Tuning the Electronic Structure of Solids by Means of Nanometer-sized Microstructures

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1. INTRODUCTION

The correlation between the properties of solids and their structure is fundamental for Solid State Physics and Materials Science. This correlation applies to the atomic as well as to the electronic structure. In the past, attention has been focussed primarily on the atomic structure and/or the microstructure of solids in order to vary their properties. In fact, several methods such as melt spinning, implantation, ball milling or cluster-assembling have been developed to synthesize materials with new atomic structures, new microstructures and, hence, new properties. It is the common feature of all materials resulting from these procedures that they are electrically neutral, i.e. their positive and negative electric charges are balanced. The modification of the properties of solids by deviating from charge neutrality has received remarkably little attention so far, although it is well established that the properties (e.g. the optical, magnetic, chemical properties, etc.) of electrically charged clusters deviate significantly from the ones of their electrically neutral counterparts (Henglein, 1979 and 1997). In fact, solids with nanometer-sized microstructures may open the way to generate materials with an excess or a deficit of electrons or holes of up to about 0.3 electrons/holes per atom (Gleiter, 2001). Such deviations from charge neutrality may be achieved either by means of an externally applied voltage or by space charges at interfaces between materials with different chemical compositions (or combinations of both). As many properties of solid materials depend on their electronic structure, significant deviations from charge neutrality result in materials with new, yet mostly unexplored properties such as modified electric, ferromagnetic, optical, etc. properties as well as alloys of conventionally immiscible components or materials with new types of atomic structures. Existing and conceivable new technological applications of solids deviating from charge neutrality will be discussed.

2. CONTROLLED MODIFICATION OF THE ELECTRONIC STRUCTURE OF NANOCRYSTALLINE MATERIALS BY APPLYING AN EXTERNAL VOLTAGE

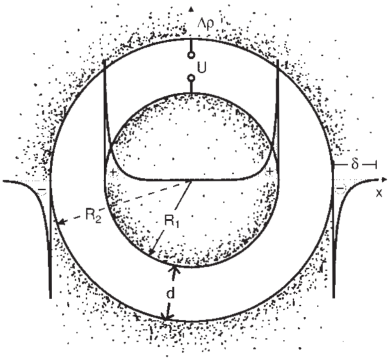

Figure 1 Schematic cross-section through a spherical capacitor consisting of spheres with radii R_1 and R_2. The applied voltage, U, causes a charge transfer between both spheres. The excess charge (+) of the inner sphere and the charge deficit (-) of the outer sphere are limited to regions with a thickness δ. Δρ indicates the excess charge density, e.g. the excess electrons as a function of the radius, x.

Let us start (Fig. 1) by considering a spherical capacitor of two chemically identical crystals (e.g. two identical metal or semiconductor crystals with mobile charge carriers, e.g. mobile electrons). If an external voltage (U in Fig. 1) is applied, it results in a charge transfer from one crystal to the other. With the polarity assumed in Fig. 1, the inner sphere carries an excess charge and the outer one a charge deficit. Both charges are primarily located in the spherical surface regions (thickness δ) of both crystals. δ is controlled by the screening length (Kittel, 1986; Ashcroft and Mermin, 1976) of the mobile charge carriers and may vary between one (or a few) lattice constants (in metals) and up to several thousand interatomic spacings (in semiconductors). If the radii R_1 and R_2 as well as the spacing between the spheres, d, are in the order of a few nanometers, and if the voltage applied between both spheres is a few volts, one obtains (for metals) a deviation from charge neutrality in the charged region δ as high as about 0.3

electrons per atom[1]. In semiconductors, the deviation from charge neutrality due to an applied voltage may be several orders of magnitude larger than the mobile charge carrier densities obtained by doping. Clearly, if one wants to utilize this method to generate solids deviating in their entire volume significantly from charge neutrality, the characteristic dimensions of these solids have to be comparable to the screening length δ. One way of generating solids with this kind of microstructure is indicated in Fig. 2. Fig. 2 shows a chain of interconnected nanometer-sized crystallites, the free surface of which is coated by a thin (e.g. 1nm thick) insulating layer. Chains of nanometer-sized crystallites may be prepared by means of inert gas condensation. Crystallites, grown in an inert gas atmosphere, aggregate spontaneously in the form of an interconnected network of crystallite chains. If a network of Al crystallites is exposed, for example, to an oxygen-containing atmosphere, their free surface is coated by a thin oxide layer. Subsequently, the oxide-coated crystallites may be immersed into an electrolytic bath (Fig. 2). If the chain network of crystallites is charged relative to the electrolyte by applying a voltage, U, the electron density in a surface region of thickness δ can be tuned by varying U.

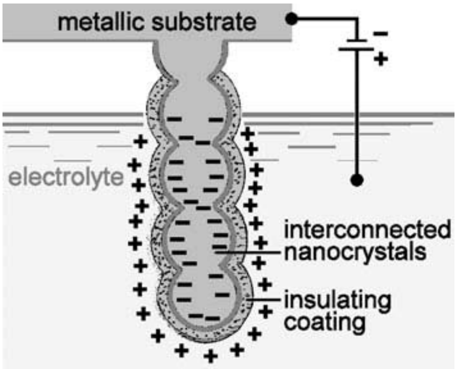

Figure 2 Chain of interconnected nanocrystals the free surface of which is coated with an insulating layer. The chain is immersed into an electrolyte. Nanometer-sized Al crystals coated with a thin (e.g. 1 nm thick) layer of Al_2O_3 are an example of this kind of a structure.

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[1] For $R_1 > R_2 - R_1 = d$ (Fig. 1) the charge deficit/excess charge, q, per atom (measured in elementary charges) in the regions δ is $q = \epsilon \cdot \epsilon_0\, U r_0 / d\delta e$. e is the elementary charge, r_0 is the average interatomic spacing in both crystals. ϵ_0 and ϵ are the dielectric constants of the vacuum and the relative dielectric constant of the material in the gap between the two crystals. For $U = 3$ V, $r_0 = 0.4$ nm, $d = 1$ nm, $\epsilon = 10$, $e = 1.6 \cdot 10^{-19}$ As, $\epsilon_0 = 8.9 \cdot 10^{-12}$ As/Vm and $\delta = r_0$, an excess charge/ charge deficit of about 0.3 electrons per atom in the surface layers of thickness δ (Fig. 1) results. In a semiconductor (with a screening length δ of about 100 r_0), the excess charge/charge deficit is about 10^{-3} electrons/atom.

In the case of metals (lattice constant about 0.4 nm) a crystallite size of about 4 nm (or smaller) is required to obtain about 50% electronically tuneable material[2]. In the case of semiconductors ($\delta \approx 10 \ldots 100$ nm), a crystallite size of 10 nm or more would be sufficient to obtain more than 50% electronically tuneable material. The insulating coating (Fig. 2) may be omitted if the conductivity of the nanocrystalline network and the electrolyte is purely electronic and ionic, respectively. In this case, a charged surface double layer results with local electric fields of up to 10^9 V/m and a correspondingly large deviation from charge neutrality. In the case of a monovalent metal, a charge deviation of up to 0.3 electrons/atom allows one to vary the number of electrons per atom in the conduction band between 0.7 and 1.3. In other words, the filling factor of the conduction band, and hence all properties related to the conduction electron density, become a tuneable quantity. This applies for example, to the dielectric function of metals, the plasmon frequency, the metal-insulator transition, all electron-electron or electron-photon interaction effects (e.g. superconductivity), the formation of excitons and polaritons, magnetic and ferroelectric properties and the interatomic interaction which, in turn, affects the atomic structure, the thermodynamic and mechanical properties as well as transport effects. In fact, in the case of semimetals (As, Bi, Sb, graphite), the electron or hole concentration per atom is in the order of $10^{-3} \ldots 10^{-5}$. Hence, semimetals may undergo a metal/insulator transition at the deviations from charge neutrality discussed here. Moreover, the close correlation between the electronic structure and the chemical properties implies that highly charged solids also deviate chemically from their electrically neutral counterparts. In fact, the synthesis of highly charged solids may be a gateway to a branch of chemistry that has received little attention so far: the chemistry of electrically highly charged solids.

Observations supporting this idea have been reported. For instance it is known that the properties of catalyst vary significantly if an external electric field is applied during the catalytic reaction. In other words, if the electronic structure of the catalyst is modified, the chemical reaction catalysed changes.

Direct experimental evidence for the modification of the band structure (and hence the related properties) of e.g. metals by an externally applied potential has been reported in the literature. For the sake of conciseness only two observations will be discussed here. Fig. 3 displays the variation of the plasmon absorption band of 5 nm Ag crystals in aqueous solution due to the chemisorption of various densities of phosphine molecules at the free surfaces of the Ag crystals (Strehlow et al., 1994). The absorption band is damped and blue shifted. This blue shift is known to result from the injection of electrons from the phosphine molecules into the conduction band of Ag (Strehlow et al., 1994). Similar interactions of various nucleophilic reagents with nanometer-sized crystallites of Ag, Pd and Ag-Hg- alloys have been reported in the past (Strehlow and Henglein, 1995; Michaelis and Henglein, 1992; Katsikas et al., 1996).

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[2] If the chain of interconnected spherical crystallites (Fig. 2) is approximated by a very long cylinder of diameter R that is charged electrically in a surface region of thickness, δ, the volume fraction, f, of the charged region relative to the total volume is given by $f = 2\delta/R$. A volume fraction of about 50% is obtained for a cylinder with a diameter of 3.2 nm, assuming $\delta = 0.4$ nm (corresponding to about one lattice constant).

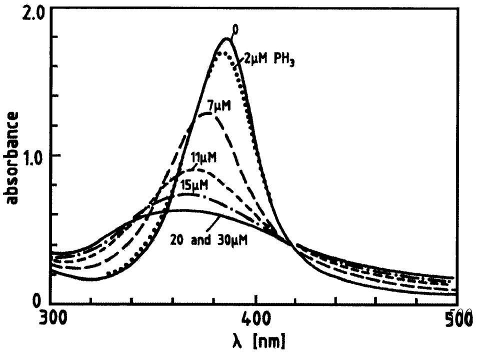

Figure 3 Absorption band of nanometer-sized silver crystals before and after the addition of various amounts of phosphine (Strehlow et al., 1994).

Direct evidence for the tuning of the electronic band structure by an applied electric field has been obtained by X-ray absorption studies. Near edge X-ray absorption fine structural studies (XANES) provide a powerful tool for the measurement of variations of the electronic structure of solids. In paragraph 3.1, XANES studies of the variation of the density of vacancies in the d-band of Pt in nanometer-sized Pt-25 at % Ru crystallites as a function of the applied electrode potential will be reported. The measurements indicate (Table I) that the density of unoccupied states in the d-band of Pt may be varied by about 20% (relatively to the electrically neutral state) if an electrode potential of 0.54 V is applied.

3. MODIFICATION OF MATERIALS PROPERTIES BY AN APPLIED EXTERNAL VOLTAGE

The availability of solids, the electronic structure of which can be tuned by applying an external voltage may open the way to tune the electron-sensitive properties of solids. Two types of property changes may be distinguished: Property changes that last as long as the external voltage is applied and subsequently vanish reversibly once the external voltage is turned off. Examples of this kind are electric, optical, ferromagnetic, dielectric and mechanical properties. Some properties of this kind will be discussed in the following three paragraphs (3.1 - 3.3). In addition to the reversible property changes, an externally applied voltage may also induce changes that are frozen-in and thus remain even when the external voltage has been removed (paragraph 3.4).

3.1 Magnetic Properties

3d-transition metals are believed to have partially filled d-bands in the metallic state. For convenience, this is often expressed by saying, the magnetization arises from holes in the 3d band. For example, the magnetization of Ni arises from 0.54

holes in the 3d band. In the case of pure Cu, the 3d band holds ten electrons and is completely filled. The 4s band of Cu can accomodate up to two electrons per atom. This means, it is half filled in Cu, i.e. Cu has one valence electron in the 4s band. If Cu is now added to Ni in the form of a Ni-Cu solid solution, electrons from the 4s band of Cu enter the holes of the 3d band of Ni and, thus, reduce the magnetic moment per atom. If 0.54 electrons are added to Ni, they will just fill the 3d band of Ni and will bring the magnetization to zero. This is the case at about 60 at % Cu in agreement with the experimental observations[3]. Let us now consider ferromagnetic materials deviating from charge neutrality in the light of this model, called the Mott-Slater model. If Ni is charged (by an applied voltage) with excess electrons, these excess electrons may - similar to the 4s electrons of Cu - fill the unoccupied 3d states of Ni. Just as in the case of Ni-Cu alloys, the changing population of the unoccupied 3d states may be expected to modify the magnetic properties of Ni in a way comparable to the alloying with Cu. If this is so, an increase (reduction) of excess electrons by an externally applied voltage should reduce (increase) the saturation magnetization and probably also vary the Curie temperature of Ni. In fact, the variation of the magnetic properties by means of tuning the electron density, may even open the way to synthesize materials in which ferromagnetism may be “switched on and off”. For instance, the ferromagnetism in Ni-Cu-alloys vanishes at about 60 at% Cu. If an alloy with this (or a similar) chemical composition is positively charged by applying an external voltage, the electrons that are removed from the alloy (due to the applied voltage) may generate unoccupied 3d-states. Hence, it seems conceivable that certain Ni-Cu alloys may become ferromagnetic if they are positively charged by an applied voltage. By returning to charge neutrality (removing the applied voltage) the ferromagnetism may be switched off again. Comparable effects are expected to apply to other ferromagnetic 3d-transition metal alloys and even to paramagnetic metals such as Pd.

A process comparable to the proposed charge-induced transformation between a ferromagnetic and non-ferromagnetic state of Ni-Cu alloys (or other 3d metals) has been reported recently (Schön et al., 2000). C_{60} fullerenes were shown to exhibit an insulator / superconductor transition if the density of mobile charge carriers is enhanced by an applied electric potentional. Fig. 4a displays the experimental arrangement used. A C_{60} single crystal with a source and drain electrode at its free surface, is covered by a thin insulating layer on top of which a gate electrode is placed. A positive gate potential (relative to the C_{60} crystal) induces a charge carrier enhancement in the C_{60} crystal of up to three electrons per C_{60} unit. At temperatures below 11 K (Fig. 4b), the C_{60} crystal became superconducting if the charge carrier density was $2{\cdot}4{\cdot}10^{14}$ e/cm^2 or higher. Superconductivity could be switched on and off by modulating the gate potential i.e. by modulating the electron density in the C_{60} crystal.

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[3] The rigid band approximation implied here is known to give an oversimplified picture, e.g. due to the formation of holes in the d-band of the majority charge carriers and the polarisation of the core electrons. In that sense, the above discussion should be considered as an outline of the general trends to be expected.

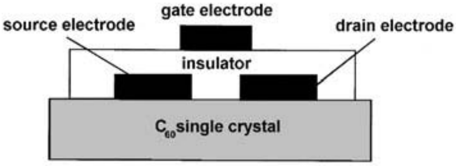

Figure 4a C_{60} device that may be switched between a superconducting and a high resistivity mode by varying the votage at the gate electrode (Schön et al., 2000).

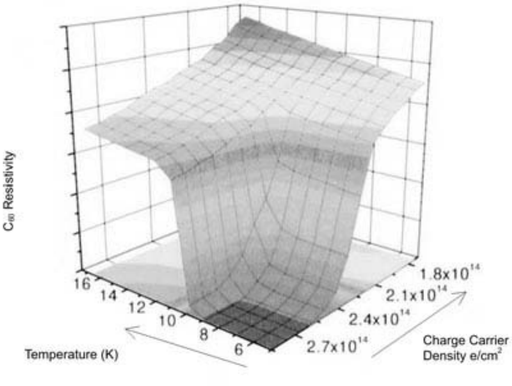

Figure 4b Resistivity of the device shown in Fig. 4a as a function of the temperature and the charge carrier density in the C_{60} crystal (Schön et al., 2000).

Direct evidence for the variation of the electron density in the d-band as a function of the applied voltage has been obtained by means of X-ray absorption studies of nanometer-sized Pt-25 at % Ru crystallites (McBean and Mukherjee, 1995).

Table 1. Results of Pt XANES measurements

Electrode potential (V)	Pt d band vacancy per atom
0.00	0.462
0.24	0.423
0.54	0.397

Table 1 summarizes the density of vacancies in the d-band of Pt in nanometer-sized Pt-25 at % Ru crystallites as a function of the applied electrode potential. The d-band vacany density was measured by X-ray absorption near edge fine structure (XANES) using the L_3 edge of Pt. A variation of the electrode potential by 0.54 V changed the unoccupied d-sites in the conduction band of Pt by no less than about 20%.

3.2 Optical Properties

An experimental set-up (Fig. 5a) which comes close to the one suggested in section 3.1 are electrochemical cells used for studying the modulation of the electroreflectance of Au or other metals (Strehlow et al., 1996). The change of the optical reflectivity of metals (Fig. 5b) upon applying a voltage to the cell is attributed to the field-induced change of the free electron density in a surface layer of the metal (Au in Fig. 5b). As was pointed out in paragraph 2, the charge carrier density in semiconductors may be varied (by up to several orders of magnitude) if an external voltage is applied. As the plasmon frequency depends on the square root of the density of free charge carriers (Lüth, 1995; Hellwege, 1976), the reflectivity of semiconductor materials may be changed reversibly (by more than one order of magnitude) by means of the applied external voltage. Semiconductors with tuneable reflectivity may be of technological interest, e.g. for displays, switchable mirrors, windows with adjustable transparency for sun-light, optical filters etc.

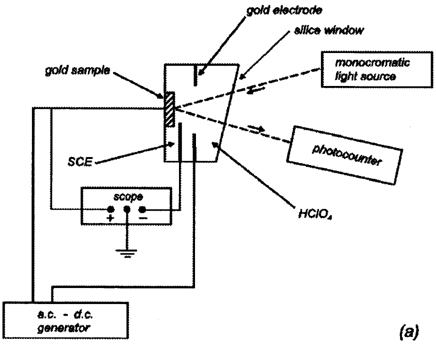

Figure 5a Schematic diagram of the experimental set-up used for electroeflectance measurement (Garrigos et al., 1973). SCE Stands for Standard Calomel Electrode.

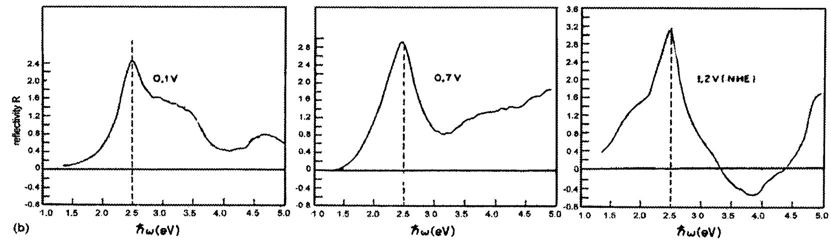

Figure 5b Reflectance, R, of Au as a function of the frequency, ω, of the light at 45° incidence measured at various potentials for in a 0.5 M H_2SO_4 electrolyte. The curves indicate the reflectance if the light polarization is parallel to the free surface of the Au crystal (Garrigos et al., 1973), cf. Fig. 5a. h is Planck's constant.

So far switchable mirrors (i.e. mirrors the reflectivity of which can be tuned by varying an external parameter) have been produced by exposing a thin (500 nm) film of Y to an atmosphere of hydrogen (Huiberts et al., 1996). At low H_2 pressures (10^3Pa or less), the Y is in the metallic state and, thus, the reflectivity for visible light is high (nearly 100%). If the H_2 pressure is increased, YH_x forms. For $x > 2$ (i.e. compositions between YH_2 and YH_3), the YH_x becomes transparent for visible light. By modulating the hydrogen pressure between 10^5 and $60 \cdot 10^5$Pa, YH_x mirrors may be switched between a reflective and a transparent mode. According to the model of Ng et al. (1997) this behaviour may be understood in terms of hydrogen induced modulation of the electronic band structure of YH_x. $YH_{3-\delta}$ ($\delta \leq 1$) may be considered as a semiconductor with localized donor states. Each donor state corresponds to one hydrogen vacancy. As long as the average spacing of the donor states is lager than the radius of the donor wave function, the material is transparent. For ($\delta \leq 0.15$) the spacing between the donor states becomes so small that their wave functions start to overlap. As a consequence, $YH_{x-\delta}$ forms a conduction band and starts to exhibit metallic reflectivity. Clearly, the tuning of the electronic band structure caused by the variation of the chemical composition (in the case of YH_x by varying the hydrogen content) it may not be the only approach. Tuning of the band structure may also be achieved by an applied electric field. For example, if the C_{60}-crystal in Fig. 4a is replaced by a suitable semiconductor, the charge carrier density in the conduction band of this semiconductor may be tuned by varying the gate voltage. As a variation of the charge carrier density in the conduction band affects the optical properties e.g. the reflectivity (Fig. 6), the optical properties of semiconductors may be tuned by an applied electric field. In fact, basically the same should also be true to metals. For example, it should be possible to shift the plasmon edge of thin layers of K, Rb, Cs etc. by an applied electric field. In other words, it should be possible to make e.g. K transparent for violett ($\lambda \approx 350$ nm) light (Hellwege, 1976).

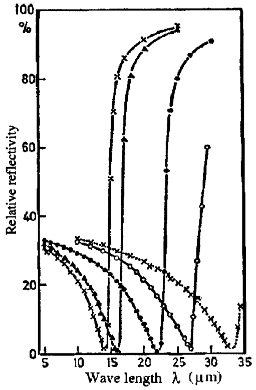

Figure 6 Reflectivity of InSb in the vicinity of the plasmon edge. The various curves represent InSb crystals with different levels of doping and hence different electron concentrations in the conduction band. The different electron concentrations result in different plasmon edge wavelengths (Hellwege, 1976).

3.3 Mechanical and Electrical Properties

The phenomenon of electrocapillarity denotes the stress and strain caused by an externally applied voltage in an electrode due to an electrochemical double layer at its surface (Bard and Faulkner, 1980). A device based on this principle has been suggested recently (Baughman et al., 1999) for single-walled nanotube sheets (SWNT). An applied potential (Fig. 7a) injects charge of opposite sign in the two pictured nanotube electrodes, which are surrounded by a liquid or solid electrolyte (background). These charges cause the nanotube to expand or contract in axial direction. A schematic edge view of a cantilever-based actuator operated in aqueous NaCl is displayed in Fig. 7b. The actuator consists of two bundles of SWNTs (shaded) that are laminated together with an intermediate layer (white region between the shaded stripes). The equality between the lengths of the two nanotube sheets is disrupted when a voltage is applied, causing the indicated actuator displacements to the left or right (Fig. 7b).

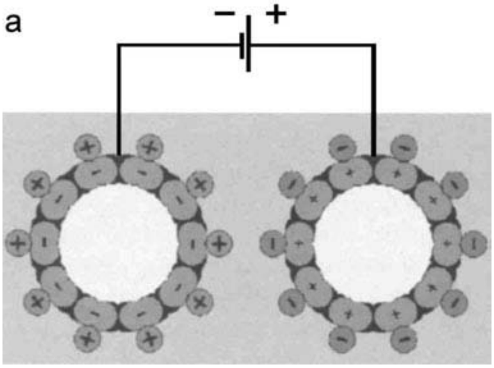

Figure 7a Schematic illustration of charge injection in a nanotube-based electrochemical actuator (Baughman et al., 1999).

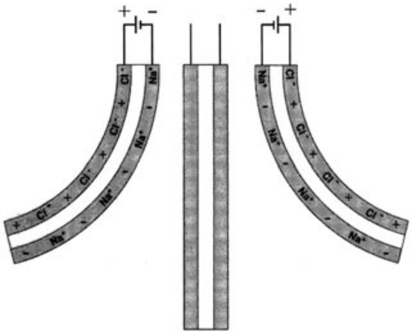

Figure 7b Schematic edge view of a cantilever-based actuator operated in aqueous NaCl (Baughman et al., 1999).

Technologically, the most important example of the controlled enhancement or depletion of the local density of charge carriers by applying an external voltage seem to be Field Effect Transitor (FET) devices. These devices consist of a source/drain electrode on opposite sides of a doped (e.g. an n-doped) semiconductor crystal and one or two gate electrodes on the side surfaces. The insulation between the gate electrode and the semiconductor crystal may be achieved either by a thin oxide (mostly SiO_2) layer (MOSFET) or by p-doping a thin region next to the gate (if the semiconductor is n-doped). The flow of electrons between the source and the drain electrode depends on the density of electrons in the n-doped semiconductor. A positive potential between the gate and the drain creates a high electron density near the gate and, thus, enhances the conductivity of the semiconductor. A negative potential between the gate and the drain reduces the electron density and, hence, the conductivity. The same principle was recently applied in order to tune the dc-conductivity of a carbon fiber that is immersed in a monomolar NaCl electrolyte. (The arrangement used somewhat similar to the one shown in Fig. 2). By varying the potential applied between the carbon and the electrolyte, the carrier density in the fiber was changed. The resistivity of the carbon fiber was noticed to be reduced if the fiber was charged positively or negatively (Fig. 8). This result may be understood as follows. The electric resistivity of a solid is essentially controlled by two factors: the density of mobile charge carrier as well as by their mean free path. If the mean free path of the charge carriers in the carbon fibers is assumed to depend little on the charge carrier density, the resistivity should vary proportional to the density of states at the Fermi energy. In the case of the carbon fibers, the density of states increases if the Fermi energy is increased or decreased relative to the neutral state by applying an

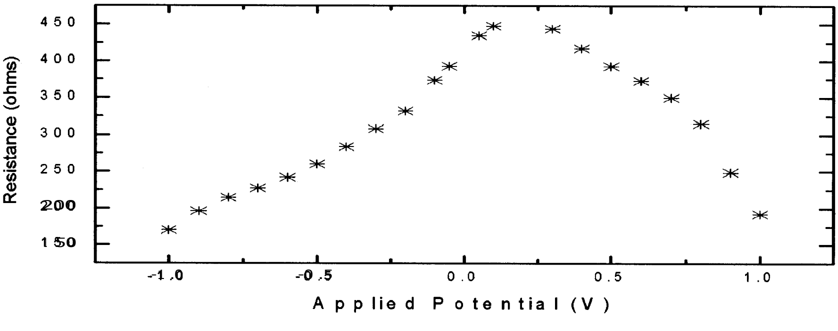

Figure 8 DC resistivity of a graphite fiber immersed in a 1 molar aqueous solution of NaCl as a function of the applied potential (Viswanath, 2000).

external potential. Hence the dc resistivity of the electrically neutral material should be higher than the one of the positively as well as of the negatively charged carbon fibers, as was observed.

3.4 Irreversible Modifications of Materials Properties Induced by Applying an External Voltage

In simple, electrically neutral metals (Pettifor, 1996), the interatomic potentials consist (in the pair-potential picture) of a hard core repulsive contribution, an attractive nearest neighbour component and an oscillatory long-range potential. In transition metals, the cohesive energy and the crystal structure are dominated by the d-bond contribution. In metals deviating to an increasing extent from charge neutrality, the Coulomb repulsion between the ion cores will become more and more significant for the interaction potential. Thus, the Coulomb repulsion will affect the crystal structure with increasing deviation from charge neutrality. In other words, the stable crystal structures of highly charged metals may deviate from the ones of electrically neutral metals. The crystal structures corresponding to the electrically charged state may be frozen-in by heating highly charged nanometer-sized crystals to elevated temperatures. At elevated temperatures, they may transform (e.g. by diffusive processes) into the crystal structure corresponding to the charged state. This structure may be preserved by cooling the charged, structurally transformed crystallites to low temperatures. So, even if one returns at low temperatures to charge neutrality, the metals and alloys will remain in the structure corresponding to the charged state. This procedure may open the way to synthesize elements and alloys with atomic structures and, hence, properties that are not yet available. Direct evidence for the coupling between the interatomic forces and the deviation from charge neutrality was recently obtained by measuring the lattice constant of 10 nm Pt crystals as a function of the applied potential i.e. the excess electric charge (Fig. 9). The experimental arrangement used corresponding basically to the one shown in Fig. 2. The excess/reduced charge per atom at an applied potential of ±1 V (Fig. 9) was measured to be about ±0.3 electrons per Pt atom in the electrically charged layer at the surface of the Pt crystals. The excess/reduced charge changed the lattice constant of Pt by up to 0.1% although the Pt crystals were much larger than the electronic screening length of Pt. In other words the pressure excerted by the thin, electrically charged surface layer (thickness 1 nm or less) is so high that it changes the lattice constant of the entire particle with a diameter of about 10 nm by 0.1%.

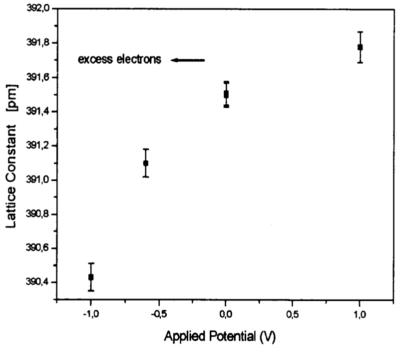

Figure 9 Variation of the lattice constant of 10 nm Pt crystals in a 1 molar KOH electrolyte as a function of the applied potential (Viswanath et al., 2001). The excess charge/ charge deficit resulting from an applied potential of ±1 V is about 0.3 electrons per Pt atom in the electrically charged surface layer of the Pt crystals.

4. MODIFICATION OF THE ELECTRONIC STRUCTURE OF MATERIALS BY INTERFACIAL SPACE CHARGE REGIONS

The thermodynamic equilibrium at interfaces requires the electrochemical potentials on both sides of the interfaces to be identical. In the case of an interface (called a heterophase boundary) between two crystals with different chemical compositions, the chemical potential difference is balanced by an electrostatic potential in the form of an electrically charged layer on either side of the heterophase boundary (the so-called space-charge layer, Fig. 10a). Hence, by analogy to the charging of solids by an externally applied voltage (Figs. 1 and 2), the built-in space charges at heterophase boundaries may be utilized to generate materials that deviate from charge neutrality. Here again, the basic idea is to incorporate such a high density of space charge regions (by means of a high density of heterophase boundaries) that their volume fraction approaches 50% or more of the total volume of the material. In fact, a volume fraction of 50% or more of electrically charged material is achieved, if the crystal size of a polycrystalline material (consisting of equal volume fractions of crystals with different chemical compositions and similar size) becomes comparable to the width of the space charge region (Fig. 10a). Polycrystals made up of nm-sized crystals with different chemical compositions are called nanocomposites. In other words, the "electronic microstructure" of nanocomposites deviates from the one of a coarse-grained polycrystal. In a coarse-grained polycrystal, the crystallites are electrically neutral because their diameters are very large in comparison to the thickness of the space charge zones. Direct evidence of the intrinsically charged state of nanocomposites due to space charge effects has been deduced (Kreibig et al., 1999), for example, from optical measurements (Fig. 10c). The extinction observed for 2 nm Ag crystals embedded in a C_{60}-matrix suggests the 2 nm Ag crystals to be electrically charged by about 0.2 electrons per Ag atom (curve C in Fig. 10c). In the case of metallic nanocomposites (Fig. 10a), the space charge regions between chemically different metals are limited to zones of about one or a few lattice constant thickness on either sides of the metallic interphase boundaries and has been revealed directly for Pd/Fe interfaces (Fig. 10b).

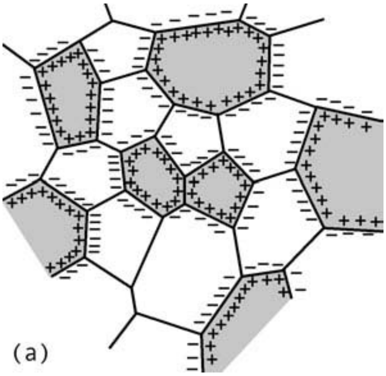

Figure 10a Space charge distribution in a nanocrystalline composite consisting of two metallic components with different chemical compositions (e.g. Ag and Fe crystals). The two components are indicated in the form of open and shaded areas.

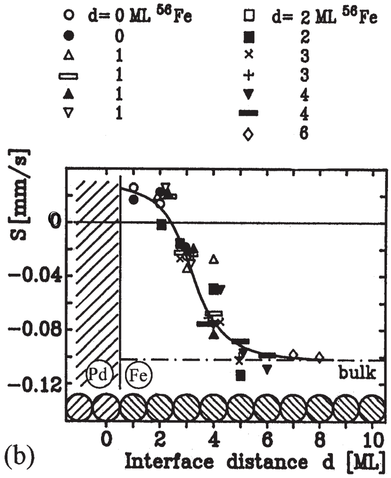

Figure 10b Dependence of the Isomer Shift, S, measured by Conversion Electron Moessbauer Spectroscopy in Fe as a function of the distance from an α-Fe(100)/Pt interface (Kisters et al., 1994). The Isomer Shift measures the difference between the total electron density at the nucleus of the Moessbauer absorber and the Moessbauer source. In the first 4 monolayers (ML in Fig. 10b), the electron density differs from the density in bulk Fe indicated by the broken line.

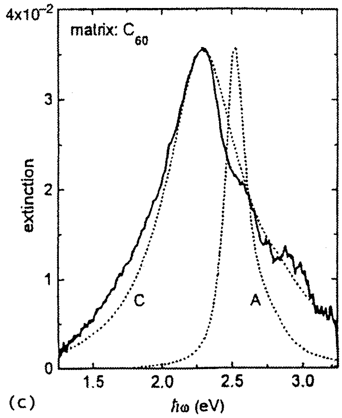

Figure 10c Measured optical absorption of silver clusters embedded in a solid C_{60}-film (Kreibig et al., 1999). For analysis, Mie spectra were calculated (curve A) with bulk dielectric properties of Ag, and if the conduction electron density in the silver clusters is reduced by 20% relative to the one in bulk Ag (curve C).

4.1 Synthesis of New Phases

Electron Phases. About 75 years ago, Hume-Rothery indicated the possibility that certain phases possess the same crystallographic structure if the number of valence electrons per atom, e/a, are comparable (electron phases). In fact, for example, the β-brass structure was found to be associated with e/a = 1.50 whereas the γ-brass and ϵ-brass structures corresponded to 1.62 and 1.75, respectively. As was pointed out previously, in metallic nanocomposites, the electronic structure in a relatively large volume fraction of the material differs from the one of the bulk due to space charge effects. If one or several of the components of a nanocomposite are Hume-Rothery phases, the deviation of the electronic structure in the space charge regions may render the structure of the Hume-Rothery phases to become unstable and transform into structures that correspond to the local (e/a) values inside of the space charge region.

Extended Solute Solubility. The modification of the electronic structure due to space charge effects in the vicinity of the interphase boundaries of nanocomposites may be one of the reasons for the observation that chemical components may form solid solutions in nanocomposites whereas the same components are found to be immiscible in the bulk. A remarkable case of this kind was reported for Ag-Fe nanocomposites (Herr et al., 1990). The Moessbauer spectrum (Fig. 11a) together with the results of X-ray diffraction experiments showed that in a region (about 4 atomic layers thick) on both sides of the interphase boundaries between the Ag and the Fe crystals, a Ag-Fe solid solution is formed (Fig. 11b). Thermodynamically, the formation of a Ag-Fe solid solution seems remarkable as Ag and Fe are immiscible in the solid and even in the molten state at temperatures close to the melting point. The solubility of Fe in Ag and vice versa may, however, be understood in terms of the electric space charge at the Ag/Fe interphase boundaries. Due to the different work functions of Ag and Fe, a space charge region results at Ag-Fe interphase boundaries. This space charge modifies the Fe electronically towards Co (Fe will be negatively charged) and Ag towards Pd (as the space charge in Ag is positive). As Pd and Co are miscible in the solid state, one might speculate that the space charge layers on both sides of the Fe-Ag interphase boundaries may enhance the solid solubility of both components.

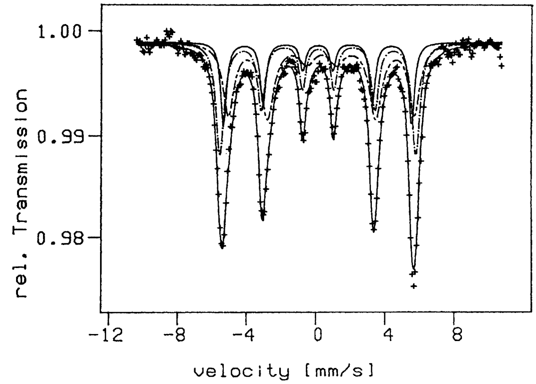

Figure 11a Moessbauer spectrum (-+-+-+-) of a nanocrystalline Fe-Ag alloy (30 at % Fe, 10 K, crystal size 8 nm). The spectrum contains of the following two components. Fe atoms dissolved in the Ag-crystals (-•-•-) and Ag atoms dissolved in α-Fe-crystals (---) (Herr et al., 1990).

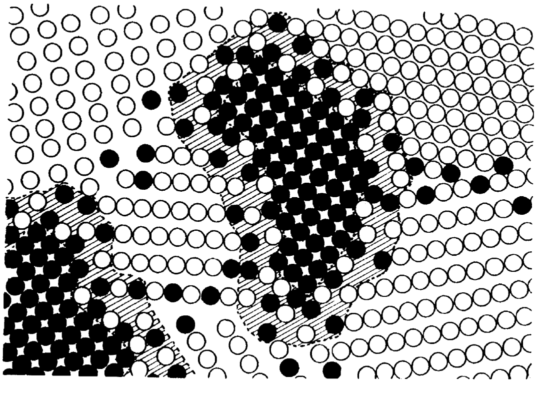

Figure 11b Schematic atomic model of the structure of Fe-Ag nanocomposits. In the region of Ag/Fe interphase boundaries, Ag-Fe-solid solutions are formed. The open and closed circles represent Ag and Fe atoms, respectively (Herr et al., 1990).

In fact, a recent survey covering 34 binary alloy systems with extended or continuous solute solubility and of 21 binary systems with no measurable equilibrium solubility in the solid state revealed a correlation between the difference of the Fermi energies of the two components of a binary alloy and their solute solubility. About 90% of the alloy systems with extended or continuous solute solubility were characterized by a small (≤2.5 eV) difference of the Fermi energies of both components, whereas about 80% of the immiscible systems exhibited significantly different Fermi energies (≥4 eV) of both partners. However, if the immiscible systems are prepared in the form nanocomposits, an enhanced solid solubility was noticed. This observation may be understood in terms of the modified electronic structure at the interphase boundaries (Fig. 10a). The space charge in the vicinity of the interphase boundaries adjusts the Fermi energies of both components. Hence in terms of the criterion that a small Fermi energy difference, promotes solute solubility an enhanced solute solubility might be expected in the space charge region at the interphase boundaries where the Fermi energies coincide.

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