MAGNETISM OF NANOSTRUCTURES

K. Bennemann
Institute of Theoretical Physics FU-Berlin Arnimallee 14, 14195 Berlin

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Contents

Summary

Characteristic results of magnetism in small particles and thin films are presented. As a con sequence of the reduced atomic coordination in small clusters and thin films the electronic states and density of states modify. Thus magnetic moments and magnetization are affected. Results are given for single transition metal clusters, cluster ensembles and thin films and tunnel systems.

1. Introduction

Due to advances in preparing small particles, thin films, film multilayers and tunnel junctions the area of nanostructures in physics has received increased interest. Clearly in engineering on an atomic scale condensed matter offers many possibilities regarding new physics and technical applications.

Of particular interest is the occurrence of magnetism in nanostructures like single transition metal clusters (Ni, Co, Fe etc.), ensembles of such clusters, for example in lattice like arrangements, ferromagnetic thin films, multilayers of such films and tunnel junctions. The latter are of interest, for example, regarding switching of electric, charge and spin currents. Size and orientation of magnetic moments and magnetization depend in general sensitively on atomic environment, atomic coordination (surfaces, interfaces etc.).

Of course, one expects that magnetic fluctuations are significant due to the reduced dimension of nanostructures. Regarding magnetic anisotropy, this will play an important role in general and also with respect to the role played effectively by the magnetic fluctuations. Due to magnetic anisotropy phase transitions occur in reduced dimensions and ultrathin films.

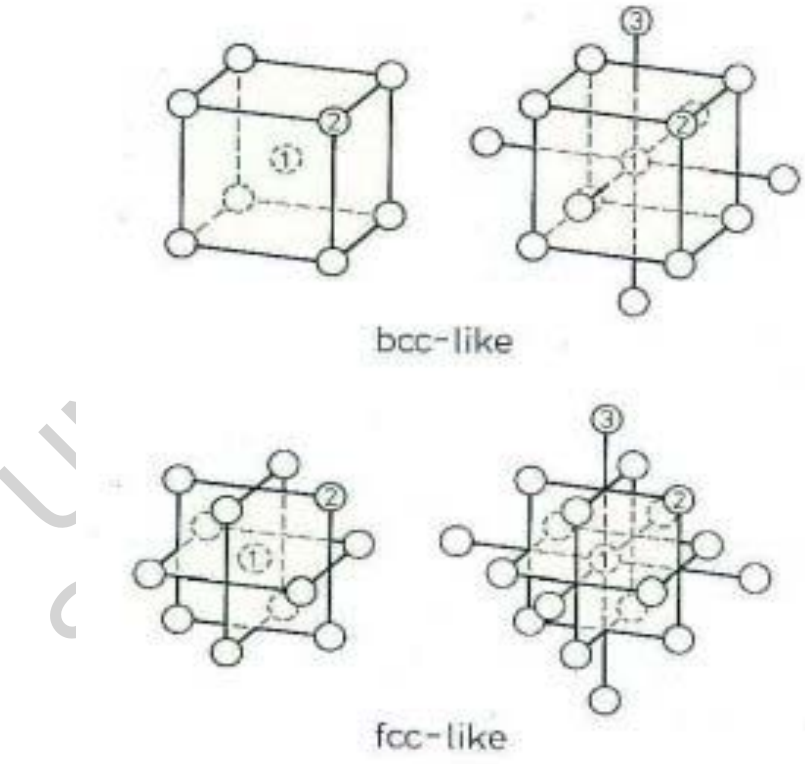

Figure 1. Illustration of b.c.c.– and f.c.c. like clusters. Different atomic shells are labeled by 1, 2 etc.

In general, the topology of the nanostructure affects strongly the electronic structure and the orientation of the magnetization, its domain structure, and magnetic relaxation. The electron energy spectrum gets discrete and quantum well states (QWS) occur in the films.

Note, in nanostructured thin films magnetic domain structure is frequently present and the reversal of a domain magnetization may be relatively slow.

In growing thin films interesting nonequilibrium behavior may result from the interdependence of atomic morphology of the nanostructure and its magnetic domain formation. This may be seen observing time resolved properties of growing nanostructures. Thus, it is of interest to study, time resolved, the occurrence of uniform ferromagnetism in thin films as a function of film thickness and domain density and size, in general on growth conditions for producing nanostructures.

In the following magnetic nanostructures having different geometry are discussed.

1.1. Magnetic Clusters

While small clusters may have a complicated atomic structure, this will tend to become bulk like for larger ones. Hence, approximately one may assume first liquid like structures as the number of atoms N in the cluster increases and then bulk like structures for larger clusters. The cluster volume V is given by $V \sim N^3$ and the surface area by $S \sim N^{2/3}$.

In Figure1 f.c.c.-and b.c.c. like cluster structures are shown. These may approximate magnetic transition metal clusters.

In Figure 2 the discretization of the electron energy spectrum of such clusters is illustrated. Levels are occupied up to the Fermi-level ε_{F} and interesting odd, even effects occur as a function of cluster size (number N of atoms).

The magnetism of the cluster is characterized by its atomic shell (i) dependent magnetic moments $\mu_i(N)$, by the magnetization M(T,N) and Curie-temperature $T_{\mathrm{c}}(N)$. These magnetic properties may be calculated using an electronic theory and for example a tight–binding Hubbard like Hamiltonian, or on a more phenomenological level a Heisenberg Hamiltonian including magnetic anisotropy. Thus, one may estimate the Curie–temperature from

$$T_{\mathrm{c}} \sim a\, J\, q_{\mathrm{eff}}(N), \qquad (1)$$

Where a is a fitting parameter, J the interatomic exchange coupling integral and q_{eff} the effective coordination number.

In Figure 2 size effects of the electronic structure are sketched. Note, screening of Coulombic interactions and width of d–electron states varies with cluster size and affects thus magnetic activity. Also spacing of the electronic states is

$$\delta \approx \varepsilon_{\mathrm{F}}/n \approx \left(\hbar v_{\mathrm{F}}/R\right)\left(k\left(F\right)R\right)^{-2}\left(N\left(0\right)V\right)^{-1}. \qquad (2)$$

Here, ε_{F} is the Fermi energy and v_{F} and k_{F} the corresponding Fermi velocity and wave–vector. V refers to the volume and $N\left(0\right)$ to the density of states (D.O.S.) at ε_{F}.One expects for $T > \delta$ that the discretization plays no great role.

The local electron density of states of atom i is given by $N_i\left(\varepsilon, N\right)$.This determines occurrence and size of local magnetic moments. Their direction is determined by magnetic anisotropy. Note, besides spin magnetism also orbital one occurs and is typically enhanced compared with bulk one.

Mie–scattering by spherical small particles is an interesting phenomena. One expects that magnetism leaves a characteristic fingerprint on the Mie–scattering profile. The magnetic field of the incident light couples to the cluster magnetization. This affects the Mie scattering in particular the backscattering intensity.

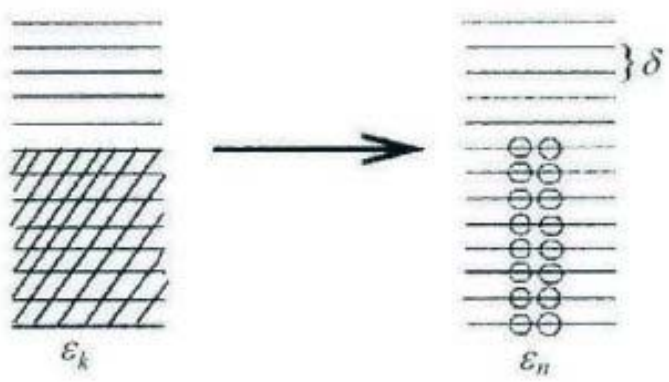

Figure 2. Sketch of size effects in small clusters having a diameter R and n electrons with energy ε_n. The spacing of the electronic energy levels is δ.

This effect of magnetism on Mie scattering needs be studied more. It offers an interesting alternative to deflection experiments by a magnetic field regarding study of small particle magnetism.

In Figure 3 an ensemble of clusters (or quantum dots) arranged in a lattice is shown. In general the lattice sites may be occupied by ferromagnetic (or paramagnetic) clusters or may be empty. Dependent on the cluster pattern one gets rich physical behavior. For example, while the single clusters are ferromagnetic, for larger spacing between the clusters one might get no global magnetization of the whole cluster ensemble. For dense spacings of the grains, dots and sufficient strong interaction amongst them, local and also global magnetization may occur as a function of temperature T. Note, typically $T_{\mathrm{C}i}\left(N\right) > T_{\mathrm{C}}$, where i refers to the cluster i and T_{C} to the Curie–temperature of the ensemble, cluster lattice.

In general interesting phase diagrams are expected for an ensemble of magnetic grains (quantum dots). One gets for interactions $J > 0$ and $J < 0$ ferromagnetism or antiferromagnetism for the grain ensemble. For a mixture of grains, for example a mixture of super conducting and ferromagnetic ones, one may observe like for alloys interesting behavior and one may get Josephson currents between the dots and due to charge transfers odd–even occupation effects, etc.

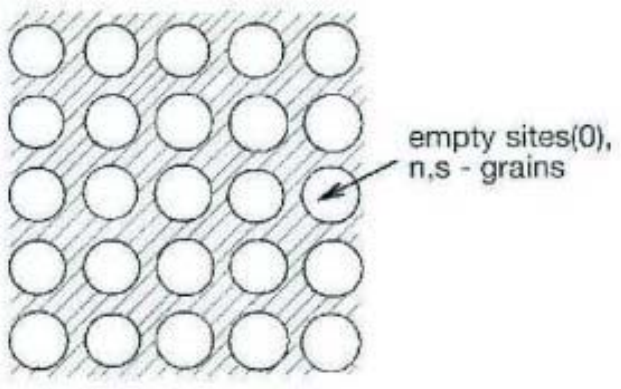

Figure 3. Illustration of an ensemble of small particles (grains) arranged in a lattice. The lattice sites may be empty or occupied by ferromagnetic, paramagnetic, or superconducting clusters, for example. Removing irregularly clusters from the lattice sites creates all sorts of nanostructures.

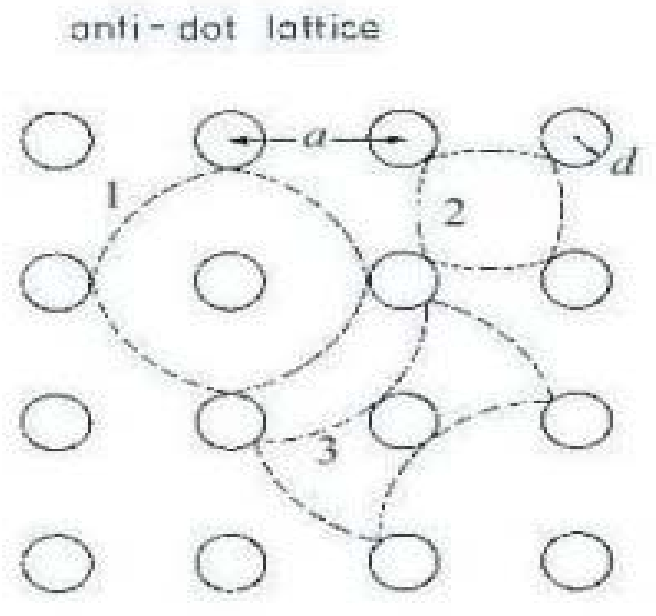

Figure 4. Magnetic field effects on polygonal electron paths in an anti–dot lattice. Here, a denotes the spacing of the anti–dots with radius d. The electrons are repelled by the anti–dot potential and thus selectively the polygonal paths 1,2,3 etc. yield the most important contribution to the spin dependent D.O.S., magnetoresistance, etc.

An interesting example of an important nanostructure is an ensemble of quantum dots, an anti-dot lattice for example. In Figure 4 an anti–dot lattice immersed in a medium is sketched. Here, the anti–dots repel electrons moving for example between the quantum dots. An external magnetic field B will change, deform the electron orbits spin–dependently and this may yield interesting behavior of the electronic properties of the system. Sensitive quantum mechanical interferences appear in such nanostructures.

In summary, these are some cluster like nanostructures. Regarding magnetism transition–metal and rare–earth atoms, metal–oxides etc. are particularly interesting. The dependence of magnetic spin and orbital moments and spin correlations on particle size and temperature are of interest. Magnetic moments, Curie temperature and magnetization control the magnetic behavior.

1.2. Film

For ultrathin films one may get magnetic behavior which could differ drastically from the one for thick ferromagnetic films. The latter are approaching as a function of film thickness d the bulk behavior (b), for the Curie–temperature $T_{\mathrm{C}}(d) \to T_{\mathrm{C,b}}$ as film thickness d increases. In ultrathin films, one or two atomic layers thick, ferromagnetism results from magnetic anisotropy (spin–orbit coupling etc.) suppressing two–dimensional magnetic fluctuations.

Various film structures are shown in Figure 5. Neighboring magnetic films may order parallel or antiparallel. Approximately, first for ultrathin films $T_{\mathrm{C}}(d) \sim d$ typically. As the thickness of the film increases the Curie–temperature approaches the bulk one. Generally one gets for multilayer structures a rich variety of magnetic phase diagrams.

Magnetic anisotropy controls the orientation of the magnetization, $\vec{M}(T, d, ...)$, at the surface of the film. Dependent on temperature T, film thickness and structure and effective magnetic field $\vec{B}$ the orientation of the surface magnetization $\vec{M}$ may change from perpendicular $M_{\perp}$ to parallel one $M_{\|}$, $M_{\perp} \to M_{\|}$. This reorientation transition, important for example for magnetic recording, is illustrated in Figure 6.

Obviously, the orientation of the magnetization at surfaces is related to the magnetic domain structure occurring in thin films. This is also clear from the illustration of domain structure in Figure7.

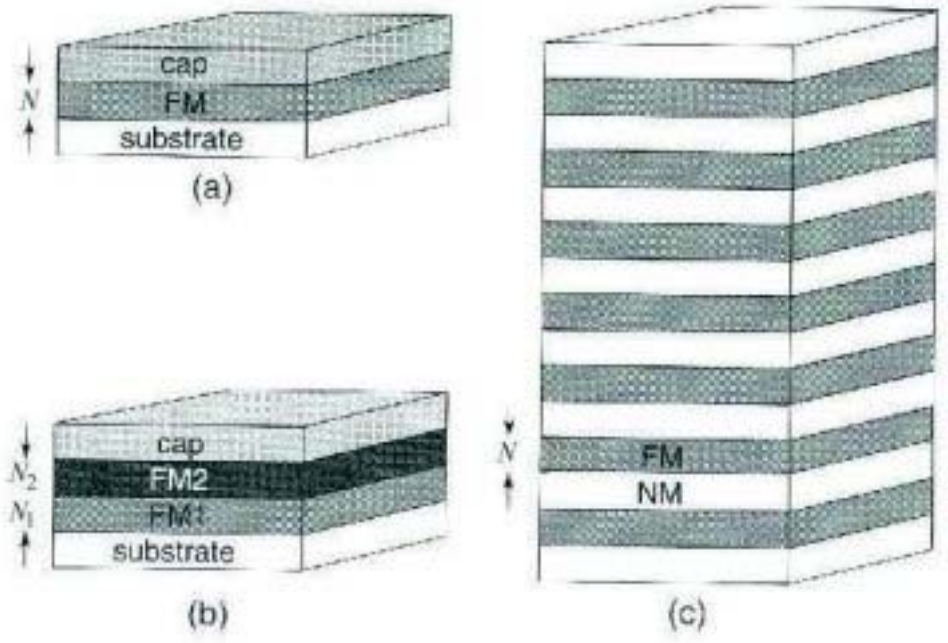

Figure 5. Thin magnetic film structures are shown. Typical configurations are given. (a) Thin ferromagnetic film of thickness *N* on a substrate, (b) two ferromagnetic films (FM1, FM2) on a substrate and (c) multilayer film structure. The ferromagnetic films are separated by a non-magnetic one (NM). At the surface the magnetic film may be covered by nonmagnetic material (cap). Of particular importance is the interplay of magnetic thin films of film multilayers.

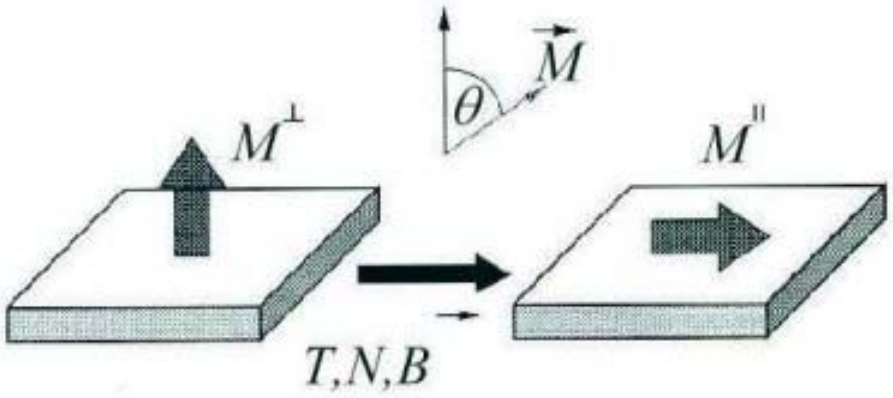

Figure 6. The reorientation transition $M_{\perp} \rightarrow M_{||}$ of the magnetization at the surface or interface is shown. This transition may be induced by temperature, increasing film thickness and film morphology and external magnetic field *B*.

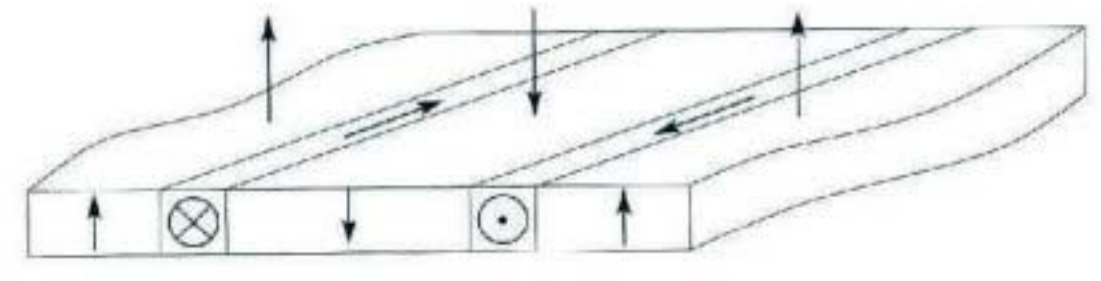

Figure 7. Illustration of a magnetic stripe domain phase of a thin film. Neighboring domains are antiferromagnetically oriented and separated by Bloch type domain walls. The magnetic structure is generally controlled by the film morphology and magnetic anisotropy. Of course, dependent on this other domain structures may result.

As expected on general physical grounds, dependent on film growth conditions one gets for thin film growth on a substrate a variety of nanostructures. This is illustrated in Figure8. For a growing film the accompanied magnetism may not be at equilibrium, but changing as the film topology changes. One has a nonequilibrium situation and magnetic structure changes due to magnetic relaxation. The latter may be relatively slow. Various patterns of magnetic domains occur in general. Then reversal of local domain magnetization occur on a ps (picosecond) to ns (nanosecond) time scale and change the global film magnetization as function of time.

Similarly as in the case of cluster ensembles on a lattice the magnetic domains resulting in nanostructured films may be dense or separated by larger distances. Correspondingly the domains are dominantly coupled via exchange or dipolar interactions, for example. This then will be reflected in the global magnetization, size of magnetic domains and in particular magnetic relaxation during film growth.

In Figure9 the growth of a thin film resulting from atom by atom deposition at the surface is shown. For simplicity fast diffusion of chemisorbed atoms is assumed. Growing of a film occurs, since deposited atoms prefer to sit next to already deposited atoms thus gaining optimally cohesions. As time progresses islands of deposited atoms coalesce and nanostructured film is formed. Of course, via diffusion of the deposited atoms the film structure depends somewhat on the film structure of the substrate. Thus, one may get island formation, striped structures and quasi uniform growth.

Regarding magnetization this reflects the nanostructure and typically magnetic domains occur before global uniform film magnetization is present.

In thin films one expects quantum-well states (Q.W.S.) which will change characteristically with film thickness. Magneto-optics (S.H.G.: Second harmonic light generation) will reflect this sensitively. Thus magnetic nano film structures (affecting the generally spin split quantum-well states) will reflect this and yield interesting optical properties. This is illustrated in Figure10.

This summarizes then interesting nanostructures consisting of films. Film multilayers

offer particularly interesting magnetic pattern. During film growth magnetic relaxation controlled by anisotropy plays an important role. This is reflected in the nonequilibrium magnetization of the film and its relaxation towards the equilibrium one.

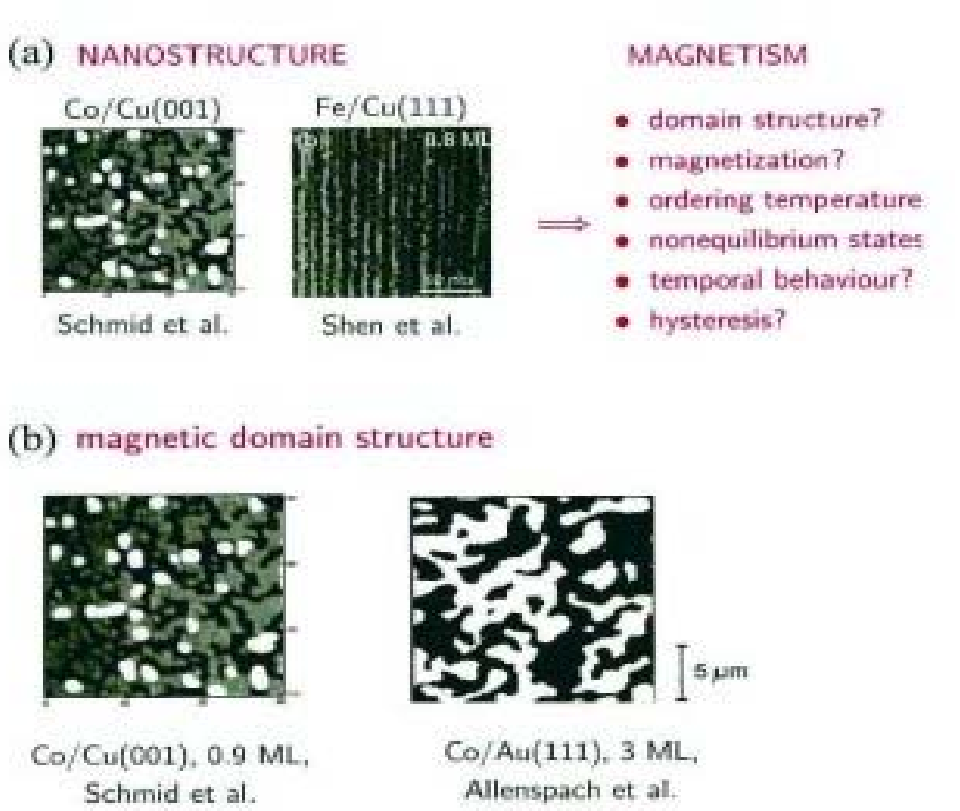

Figure 8. Nanostructures of ultrathin films and accompanying magnetic domain structures. The upper Figure (a) shows various observed nanostructures and questions are listed regarding dependence of the resulting magnetic structures on film topology. (b) The obtained magnetic domain structures are given. Only domain structure at surface is shown. The domains (white) have a perpendicular magnetization. Note, such structures are observed in various experiments.

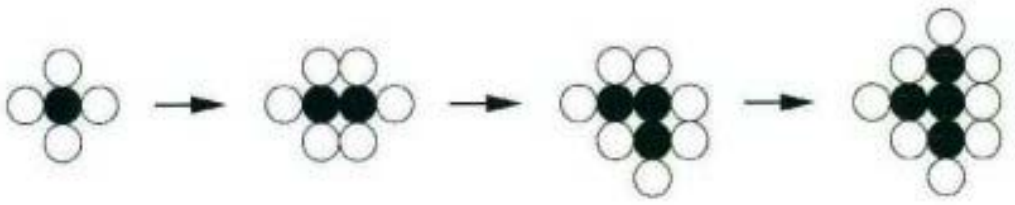

Figure 9. Illustration of simple (Eden type) growth of a thin film (for a square lattice). One assumes fast surface diffusion and uses a Monte Carlo simulation of molecular beam epitaxial (MBE) film growth. Surface atomic sites are indicated. Deposited atoms are given in black and due to cohesive energy prefer to cluster.

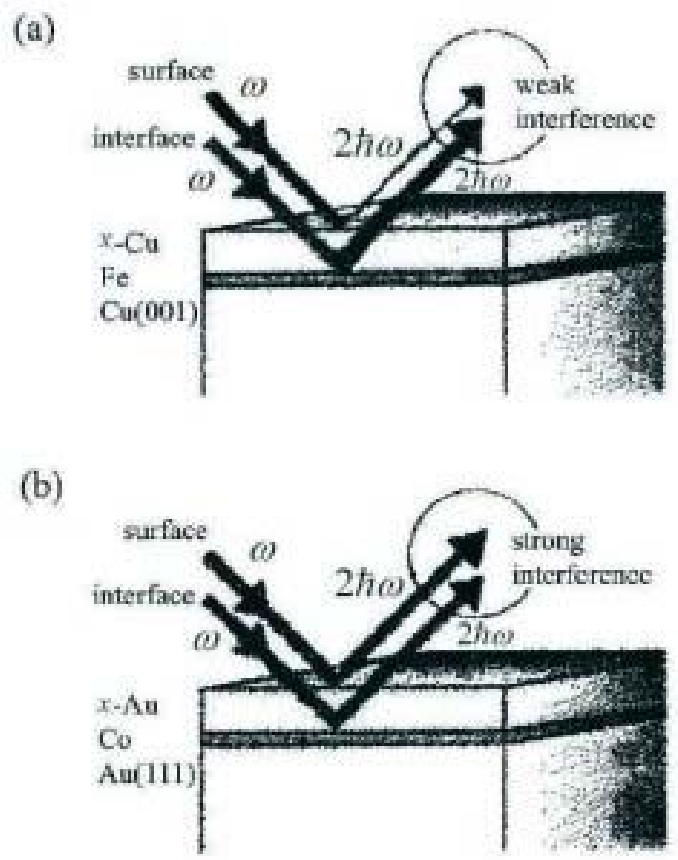

Figure 10. Illustration of magnetic S.H.G. resulting from thin films with Q.W.S.. Note, in magnetic films the Q.W.S. are spin polarized and their energies depend on film thickness. Thus, Q.W.S. involved in SHG cause film thickness dependent effects and oscillations in magneto-optical signals. The interference of S.H.G. from the surface and the interface (film/substrate) yields a sensitive detection of magnetism. Characteristic differences occur for (a) weak interference, (b) strong interference.

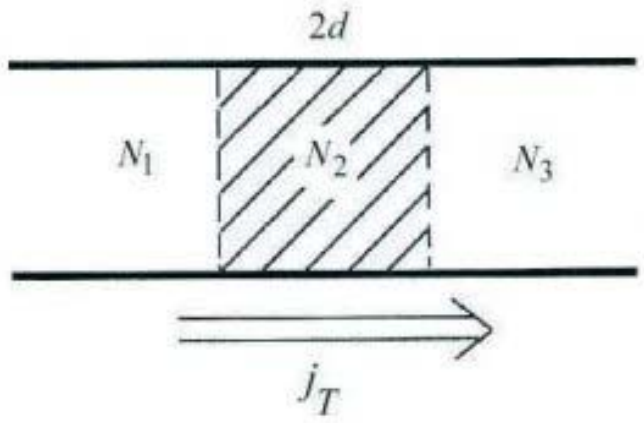

Figure 11. A tunnel junction $N_1 \big| N_2 \big| N_3$, where N_i refers to the state, magnetic,

superconducting, normal. The current j_T may refer to spin- or charge transport and may be driven by the phase difference $\Delta\varphi = \varphi_3 - \varphi_1$, for example. Note, applying a voltage V to the system may yield a two-level system (resembling a qubit, etc.)

1.3. Tunnel Junctions

Tunnel junctions are interesting microstructures, in particular regarding quantum mechanical behavior, switching devices and charge- and spin currents and their interdependence. Coupling of the order parameter phases on both sides of the tunnel medium yields Josephson like (spin) currents. Obviously, this will depend on the magnetic state of the medium through which tunneling occurs. This is sketched in Figure 11.

Clearly tunneling allows to study magnetic effects, ferromagnetic versus antiferromagnetic configurations of the tunnel system ($\uparrow|T|\uparrow$, or $\uparrow|T|\downarrow$,) and for example interplay of magnetism and superconductivity ($T \equiv S.C.$). Also importantly, tunnel junctions may serve to study Onsager theory on a molecular{atomistic scale.

In summary, for illustrating reasons various interesting nanostructures like clusters, films and tunnel junctions with important magnetic effects are discussed. In the next chapter some theoretical methods useful for calculations are presented. Then results obtained this way are given.

It is important to note that for illustrational purposes the physics has been simplified and that the analysis can be improved. However, likely this will not change the physical insights obtained from the simplified analysis. For more details see for clusters studies by Pastor *et al.* and by Stampfli *et al.*, and for films research by Jensen *et al.*, and for tunnel junctions studies by Nogueira, Morr *et al.*.

2. Theory

In general theory for nanostructures must allow for a local, atomic like analysis of the electronic structure. Using Hubbard Hamiltonian and tight-binding type theory one may determine

a) $N_{i\sigma}(\epsilon,\ldots)$, the electron density of states at an atomic site i and for spin σ, dependent on the local atomic configuration surrounding atom i,
b) μ, the atomic like magnetic moment, as a function of particle size (cluster size or film thickness),
c) *M*, the magnetization and the Curie-temperature (T_C). Note, all properties result from the electronic Green's function $G_{i\sigma}(\epsilon,\ldots)$.

Including spin{orbit coupling (V_{so}) yields magnetic anisotropy. Thus, also

d) Orbital magnetism is obtained. Note, anisotropy and orbital magnetism get typically for nanostructures more important.

Alternatively to an electronic theory one may use on a more phenomenological level the Heisenberg Hamiltonian including magnetic anisotropy to analyze magnetism in nanostructures.

2.1. Electronic Theory

To determine the size and structural dependence of the magnetic properties of small transition metal clusters the Hubbard Hamiltonian for *d*-electrons which are expected to contribute dominantly is used (see Pastor *et al.*)

$$H = \sum_{i=j} t_{ij} c_{i\sigma}^{+} c_{i\sigma} + H', \tag{3}$$

$$H' = \sum_{i} \epsilon_{i\sigma} n_{i\sigma} - E_{dc}, \tag{4}$$

and effective on-site electron energies

$$\epsilon_{i\sigma} = \epsilon^0 + U\Delta n_i - \sigma \frac{J}{2} \mu_i. \tag{5}$$

Here, $c_{i\sigma}^{+}$ and $c_{i\sigma}$ are the usual creation and annihilation operator for electrons on size i and spin σ and t_{ij} denotes the distance dependent hopping integral. Note, i, j refer to atomic sites and includes orbital character (d_i: e_g ; t_{2g} orbitals, *s*, *p*-orbitals). H' describes interactions (in the unrestricted Hatree-Fock approximation). The effective intra-atomic Coulomb interaction are denoted by U and the exchange interaction by $J\left(J = U_{\uparrow\downarrow} - U_{\uparrow\uparrow}, U = \left(U_{\uparrow\downarrow} + U_{\uparrow\uparrow}\right)/2\right)$. Here, $U_{\sigma\sigma'}$, refers to electron spins σ, σ'. $E_{dc} = (1/2)\sum_{i,\sigma}\left(\epsilon_{i\sigma} - \epsilon^0\right) < n_{i\sigma} >$ corrects for double counting as usual. The charge transfer Δn_i is given by $\Delta n_i = n_i - n^0, n^0 = (1/n)\sum_i n_i$.

The quasi local magnetic moment at site i is given by

$$\mu_i \propto < n_{i\uparrow} - n_{i\downarrow} > \tag{6}$$

with $\langle n_{i\sigma} \rangle = \int_{-\infty}^{\epsilon F} d\epsilon N_{i\sigma}\left(\epsilon - \epsilon_{i\sigma}\right)_t$. Subscript t refers to time t Here, $N_{i\sigma}(\epsilon)$ is the density of states (DOS) at site i for electrons with spin σ.

This theory applies also to thin films. Then, *i* may refer to film layer.

To calculate the magnetization $M(T)$ one must take into account the orientation of the

magnetic moments. Assuming a preferred magnetization axis one gets (Ising model, see Moran-Lopez et al., Liu)

$$M(T) \simeq \sum_i \left\{ p_i^+ \mu_i^+(T) + p_i^- \mu_i^-(T) \right\} \Big/ \mu^+(0`). \tag{7}$$

The probabilities $p_i^{+,-}$ refer to finding moments $\mu_i^{+,-}$ pointing parallel or antiparallel to the preferred magnetization axis. For simplicity one may use the approximation $p_i^{+,-} = p^{+,-}$. Assuming spherical like clusters, then i refers to the atomic shell of the cluster and $\mu_i^{+,-}$ to the magnetic moment within shell i pointing in the direction of the magnetization (+) and in opposite direction (–), respectively.

Then one determines the order parameter $(\propto M)$

$$\mu_i = p_i^+ - p_i^- \simeq p^+ - p^- \tag{8}$$

$(\mu_i \approx \mu)$ from minimizing the free-energy

$$F = \Delta E - TS\,. \tag{9}$$

Here, the entropy S is given by

$$S \simeq -kN \left\{ p^+ \ln p^+ + p^- \ln p^- \right\} \tag{10}$$

and $\Delta E = E(\mu) - E(0)$. The electronic energy is calculated using a Hamiltonian *H*, for example Eq.(3). For calculating the Green's functions the electronic energies are determined from

$$\epsilon_{i\sigma}^{+,-} \simeq \epsilon_{i\sigma}^0 - \sigma J \sum_j \mu_i^{+,-} \mu_j^{+,-} \tag{11}$$

Note, $\epsilon_{i\sigma}^{+,-} \simeq \epsilon_{i\sigma}^0 - \sigma \mu_i^+ J \sum_j \left\{ p^+ \mu_j^+ + p^- \mu_j^- \right\}$. The Curie-temperature is given by $M(T_c) = 0$.

A similar analysis can be performed using functional-integral theory as developed by Hubbard *et al.*, see Pastor et al.

Note, this theory can also be used for films. Then i may refer to the film layer, etc..

The magnetization can be determined using the Bragg-Williams approximation.

Assuming for simplicity Ising type spins one finds for the magnetization (see Jensen, Dreyssé*et al.*)

$$M_i(T) = \tanh\left\{\beta J \mu_i \left(z_0 M_i \mu_i + z_1 M_{i+1}\mu_{i+1} + z_{-1} M_{i-1}\mu_{i-1}\right) - \Delta h_i\right\}. \quad (12)$$

Here, $\beta = 1/kT$, z_0, z_1, z_{-1} are nearest neighbor coordination numbers and Δh_i denotes the Onsager reaction field. Referring to cluster shells (film layer) z_0 gives the neighboring atoms of i within shell (layer) i and z_{-1} and z_1 the nearest neighbor atoms in the shell (layer) below and above, respectively. It is

$$\Delta h_i = (\beta J \mu_i)^2 M_i \left\{z_0 \mu_i^2 \left(1 - M^2\right) + z_1 \mu_{i+1}^2 \left(1 - M_{i+1}^2\right) + z_{-1}\mu_{i-1}^2 \left(1 - M_{i-1}^2\right)\right\} \quad (13)$$

Applying these expressions to films one has $z_1 = 0$ (and $\mu_1 = 0$) if *i* refers to the surface plane and $z_{-1} = 0, \mu_1 = 0$) if *i* refers to the film layer on a nonmagnetic substrate.

Note, for $T \le T_C$ Eq.(13) can be linearized yielding a (tridiagonal) matrix equation which largest eigenvalue gives $T_C(d)$. For the Hamiltonian H one may use the Heisenberg one, for example.

Orbital magnetism, anisotropy: Adding spin-orbit interaction V_{so} to Eq.(3), $H \to H + V_{so}$, and

$$V_{so} = -\nu \sum_{\alpha,\beta} \left(\vec{L_i} \cdot \vec{S_i}\right)_{\alpha,\beta} c_\alpha^+ c_\beta, \quad (14)$$

one may also determine magnetic anisotropy and also orbital magnetic moments $\left(\langle L_i \rangle\right)$. $\left(\vec{L_i} \cdot \vec{S_i}\right)_{\alpha,\beta}$ refers to intra-atomic matrix elements between orbitals α, β. Of course, the orbital moment $\vec{L_i}$ depends on cluster atom *i* and on orientation δ of $\vec{S}$ with respect to structural axis: $\vec{L_i} \to L_{i,\delta}$ (see Pastor *et al.*).

2.2. Heisenberg Type Theory

One may also calculate the magnetism in nanostructures by using the Heisenberg type Hamiltonian, including magnetic anisotropy (see Jensen *et al.*). Then

$$H = -\frac{1}{2} J \sum_{i,j} \vec{S_i} \cdot \vec{S_j} + \frac{1}{2} A \sum_{i,j} \left(\frac{\vec{S_i} \vec{S_j}}{r_{ij}^3} - 3 \frac{\left(\vec{S_i} \cdot \vec{r_{ij}}\right)\left(\vec{S_j} \cdot \vec{r_{ij}}\right)}{r_{ij}^5} \right) + H_{\text{anis}}\cdot,$$

with

$$H_{\text{anis.}} = -\frac{1}{4} K \sum_{i,j} S_i^z S_j^z - \frac{1}{4} D \sum_{i,j} \left(S_i^x S_j^x + S_i^y S_j^y \right). \qquad (15)$$

Here, K and D are uniaxial and quartic in-plane (exchange) anisotropy constants, respectively. Note, in H the first term is the Heisenberg exchange interaction and the second term refers to the magnetic dipole interaction, and $A = \mu_0 \left(g \mu_B\right)^2 / a_0^3$. $\vec{S_i}$ denotes Heisenberg spins (spin $\frac{1}{2}$) at site i.

Applying standard methods of statistical mechanism one gets the free-energy F, the magnetization and phase-diagrams in terms of J and the anisotropy forces for clusters and thin films and also for nanostructured films with magnetic domain structure. For a more detailed analysis see in particular P. Jensen *et al.*.

From Eq.(15) follows the magnetic reorientation transition, for example as driven by temperature:

$$\vec{M}_{|} \rightarrow_{T_R} \vec{M}_{||} \qquad (16)$$

occurring at temperature T_R. Note, the temperature dependence of the effective anisotropy parameters and of the dipole coupling is mainly determined by the magnetization. Minimizing the free-energy (anisotropy contribution to free-energy) gives the transition $M_{\perp} \rightarrow M_{||}$ at T_R.

Since the control parameters in Eq.(15) depend on atomic structure, morphology of the nanostructures, film thickness for example.

The above Hubbard-tight-binding type electronic theory and the Heisenberg type phenomenological theory including magnetic anisotropy permit a calculation of the magnetic properties of nanostructures. A basic understanding of the dependence of magnetism in nanostructures on atomic configuration and on more global morphology is obtained.

Note, for alloys one may extend above theories using appropriate versions of C.P.A. like analysis (C.P.A: coherent potential approximation).

2.3. Balian-Bloch Type Theory

The important electronic structure (shell structure) for mesoscopic systems like

spherical clusters, discs, rings, dots can be determined using a relatively simple theory developed by Stampfli *et al.* extending original work by Balian-Bloch (Gutzwiler). The dominant contribution to the electronic structure results from (interfering) closed electronic orbital paths. Then the key quantity of the electronic structure of a quantum dot system, the density of states (DOS), can be calculated from (*n* = number of atoms in nanostructure) from the Green's function G via

$$N_\sigma(E,n)=\frac{1}{2\pi i}\int_V d^d r\left\{G_\sigma(\vec{r},\vec{r}',E+i\epsilon)-G_\sigma(\vec{r},\vec{r}',E-i\epsilon)\right\}_{\vec{r}'=\vec{r}}. \quad (17)$$

One gets ($\bar{N}$ = average DOS)

$$N_\sigma(E,n)=\bar{N}_\sigma(E,n)+\Delta N_\sigma(E,n), \quad (18)$$

where ΔN_σ refers to the oscillating part of the DOS due to interference of dominating closed electron paths in clusters, thin films, and ensemble of repelling anti-dots, see the theory by Stampfli *et al.*. Clearly this scattering by the dots can be spin-dependent and can be manipulated by external magnetic fields B (s. cyclotron paths, Lorentz-force etc.).

Under certain conditions regarding the potential felt by the electrons in the nanostructures (square-well like dot potentials etc.) one gets the result (Stampfli *et al.* using Balian-Bloch type theory)

$$\Delta N_\sigma(E,n)\simeq\sum_l A_{l\sigma}(E,n)\cos(kL_l+\phi_{l\sigma}). \quad (19)$$

Here, l refers to closed orbits (polygons) of length $L, k=\sqrt{|E|+i\delta}$, and $\phi_{l\sigma}$ denotes the phase shift characterizing the scattering potential and the geometry of the system. An external magnetic field affects $\Delta N_\sigma(E,n)$ via path deformation and phase shifts resulting from magnetic flux (see Aharonov-Bohm effect).

Clearly, the DOS in particular $\Delta N_\sigma(E,n)$ will control the magnetism in various nanostructures, in quantum dot systems. For details of the Balian-Bloch like analysis see the theory by Stampfli *et al.*.

2.4. Magneto-optics

Interesting magneto-optical behavior is exhibited by magnetic films. Nonlinear optics, SHG is very surface sensitive and reflects the magnetic properties of the film. SHG is generated at the surface and at the interface surface/substrate or at the interface of two films. The nonlinear susceptibility $\chi^{(2)}$ may be split into the contribution χ^s from the surface and χ^i from the interface and owing to the contribution $\chi^s\chi^i$ to the SHG

intensity the relative phase of χ^s and χ^i is important. Furthermore, the magnetic contrast $\Delta I(2\omega, M) \propto I(2\omega, M) - I(2\omega, -M)$ will reflect the film magnetism, since the susceptibility has contributions which are even and odd in M, see Bennemann *et al.* in Nonlinear Optics, Oxford University Press. High resolution interference studies are needed to detect also magnetic domain structures of films. Also polarized light reflects magnetism and in particular the magnetic reorientation transition.

In particular, interesting magneto-optical behavior results also from the spin-dependent quantum-mechanical interference due to quantum-well states (Q.W.S.) occurring in thin films. These states result from the square-well potential representing the thin film. In magnetic films the resulting electron states are spin-split. Characteristic magnetic properties follow. In contrast to band-states only Q.W.S. show a strong dependence on film thickness. Thus, to study film thickness dependent (optical) behavior SHG involving Q.W.S. needs be studied.

Since the Q.W.S. energies shift with varying film thickness, the SHG light intensity $(I_{2\omega})$ involving these states may oscillate and this in particular may reflect the magnetism of the film. Clearly, owing to the periodic appearance of Q.W.S. at certain energies for increasing film thickness, SHG involving these states may be resonantly enhanced and then oscillations occur as a function of film thickness. A detailed analysis, see Luce, Bennemann, shows that the SHG periods depend on the parity of the Q.W.S., the position of the Q.W.S. within the Fermi{see or above, and on the interference of second harmonic light from the surface and interface film/substrate, etc. If this interference is important, then SHG response is sensitive to the parity of Q.W.S., light phase shift at the interface and inversion symmetry of the film. If this interference is not important, then SHG response and oscillations are different.

Characteristic properties of film SHG are listed in Table 1.

	$\lvert X^{\mathrm{i}}\rvert \gg \lvert X^{\mathrm{s}}\rvert$	$\lvert X^{\mathrm{i}}\rvert \approx \lvert X^{\mathrm{s}}\rvert$
k selectivity	(*x* Cu/Fe/Cu(001) for example)	
	Strong magnetic signal due to strong (magnetic) interface contributions	Weak SHG signal, from only few *k* points and without strong interface contributions
	Sharp SHG peaks due to few contributing *k* points resulting in strong resonances	Double period and additional periods are frequency dependent
	Strong frequency dependence of the SHG oscillation period due to the dispersion of the QWS in the $k_{\perp}$ direction	MOKE period absent; doubled and additional SHG period visible

	MOKE period and larger periods visible; no exact doubling of the MOKE period	
No *k* selectivity	Strong magnetic signal, since strong interface contribution	(*x* Au/Co(0001)/Au(111) for example)
	Broad SHG peaks, since contributions come from many *k* points	Broad, smooth peaks, since interference effects do not change abruptly
	Weak frequency dependence of the oscillation period	SHG oscillation periods rather independent of the frequency, since the SHG signal is caused by the QWS near E_F
	MOKE period and larger periods present	MOKE period absent, doubled period present

Table 1. Characteristics of SHG response from thin films. Its dependence on film thickness involves QWS. The SHG oscillations reflect magetic properties of the film.

The interesting S.H.G. (second harmonic light) interference resulting from surface and interfaces and reflecting sensitively magnetic properties of the film may be analyzed as follows. The SHG light intensity $I(2\omega)$ is approximately given by

$$I(2\omega) \sim \left|\chi_{ijl}\right|^2, \tag{20}$$

where χ denotes the nonlinear susceptibility. Note, χ may be split as (s: surface, i: interface)

$$\chi_{ijl}(2\omega) = \chi^s_{ijl} + \chi^i_{ijl} \tag{21}$$

One gets

$$I(2\omega) \sim 2\left|\chi^s_{ijl}\right|^2 + 2\chi^s_{ijl}\chi^i_{ijl} + \ldots \tag{22}$$

Then obviously the intensity $I(2\omega)$ depends on the resultant phase of susceptibilities χ^s and χ^i.

Then assuming, for example, that χ^s and χ^i are of nearly equal weight $\left(\left|\chi^s\right| \sim \left|\chi^i\right|\right)$, it may happen that the 2nd term in Eq.(22) cancels the first one, see for example

inversion symmetry in films $\left(\chi^{s}_{ijl} \rightarrow -\chi^{i}_{ijl}\right)$ or phase shift of the light by π at the interface.

If the interference of light from the surface and interface is negligible then different oscillations of the resulting SHG light as a function of film thickness occur. For the period of such oscillations the parity of the QWS (quantum well states) is important, see results for $I\left(2\omega\right)$ and discussion by Bennemann, *Nonlinear Optics* (Oxford).

The weight of the optical transitions $i \rightarrow j \rightarrow l$ changes as the film thickness increases, see later discussion. Thus, Moke and Nolimoke oscillations occur.

Regarding optical properties, the morphology of the thin film and its magnetic domain structure should play a role in general. For magnetic film multilayers one expects interesting interferences and magnetic optical behavior.

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Biographical Sketch

K. Bennemann Born in Münster (Westfalia,Germany),study physics, mathematics Univ.of Münster, diploma 1960 (superv Profs Franz,Tewordt),PhD Univ. of Ill.,Urbana (superv Seitz, Köhler), postdoc Univ of Ill (Prof Bardeen), Univ of Chicago (Prof Cohen, Falicov), Prof Univ of Rochester, Prof Univ FUB (since 1971), visiting Prof. Cambridge Univ (Prof N Mott), Univ Basel, ETH Zürich, Technion, Hebrew Univ., Curie Univ. Paris, and Modena, Bariloche (Argentina), Tokyo Univ., etc. Books Nonlinear Optics (Oxford Univ Press), Superconductivity(Springer), Superfluid He (Wiley), etc.
Research Ultrafast Dynamics, Superconductivity, Magnetism