Shell Effect in Exchange Coupling of Transition Metal Dots and Their Arrays

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On the basis of their electronic structure, we consider the magnetic properties of transition metal quantum dots and of arrays in which the dots are separated by nonmagnetic tunnel barriers. The oscillating size dependence of the magnetic moment of such *strong* ferromagnetic dots is well reproduced within a band structure-based shell model. If the dots are arranged in an array the analysis of the Nagaoka state of supermoments allows one to identify the conditions which lead to magnetic ordering. Our calculations compare favorably with recent experimental findings. [S0031-9007(98)07595-4]

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Advances in surface technology have made it possible to reduce the size of electronic structures until their spatial dimensions become comparable to the de Broglie wavelength of the active electrons. Interesting examples of such mesoscopic systems are atomic clusters and/or quantum dots (in the following simply referred to as quantum dots, QD) which have received considerable attention in recent years. Being a fascinating research topic in their own right (cf., e.g., Refs. [1,2]), new phenomena can be expected if the dots are arranged in an array just like atoms in a lattice. Particular effort is currently devoted to investigate the magnetic properties of such structures [3–7]; being not only candidates for advanced nanoscale storage media, they are also of fundamental interest for the study of interactions, transport processes, and phase transitions. Recent experimental work on one- (1D) and two-dimensional (2D) self-organized (i.e., quasiperiodic) arrays of nanosize transition-metal dots show magnetic ordering [4–7] mostly of the dipolar type. However, in the case of a 2D system of Fe dots on an insulator substrate a long-range order has been found [3] which has been attributed to a contribution of exchange coupling between the dot supermoments. This mechanism is expected to be of increasing importance for a 3D ordering of the dots and will also play a key role with respect to magnetotransport processes in arrays, similarly to what is observed in magnetic alloys (cf. [8]).

In the work to be reported here we treat the magnetic properties of QD arrays on the basis of their electronic structure. Thereby we proceed in two steps: we will first calculate the magnetic moment of individual dots within the electronic shell model for size-limited aggregates. In the second step, the dots are arranged in an array; tunneling exchange coupling between the dots will modify the electronic level density [9] leading to coupling of the dot supermoments into a ferromagnetic or antiferromagnetic state.

The magnetic properties of free individual transition-metal and rare-earth element dots have recently been studied experimentally [10,11] and analyzed theoretically [12–14]. For a nanosize dot at finite temperature the superparamagnetic picture (i.e., weak anisotropy) can be used [15]. In *strong* ferromagnetic materials, such as the iron series transition metals Co and Ni, with strong molecular self-field H (providing a measure of the intradot exchange interaction) the Fermi energy ϵ_F is located above the top energy $\epsilon_\uparrow$ of the majority spin levels and below the top energy $\epsilon_\downarrow$ of the minority spin band (cf., e.g., [8,16]). Then the magnetic moment per atom μ_N of a dot containing N atoms is given by $\mu_N = \mu_B n_h$, with μ_B the Bohr magneton and n_h the number of holes in the minority spin band. n_h is related to the mean number δn_s of delocalized s electrons above $\epsilon_\uparrow$ in the majority spin band [14] by $n_h = n_h^0 - \delta n_s$, with $n_h^0 = 10 - n_v + n_s^0$, where n_v and n_s^0 are the numbers of outer shell and s electrons per atom, respectively. The quantity δn_s can be expressed through the contribution ρ_s of the sp band to the level density of active electrons

$$\delta n_s = [N_s(\epsilon_F) - N_s(\epsilon_\uparrow)]/N\,,$$
$$N_s(\epsilon_i) = \int_{-\infty}^{\infty} d\epsilon\, \rho_s(\epsilon) f(\epsilon - \epsilon_i) \tag{1}$$

with $f(x) = [1 + \exp\{x/k_B T\}]^{-1}$ the Fermi function. The number of s electrons n_s^0 depends on the average coordination number of atoms in a dot and can be represented by contributions of "*bulk*" n_s^{bulk}, "*surface*" n_s^{surf}, and "*curvature*" n_s^{curv} components $n_s^0 \approx n_s^{\mathrm{bulk}} + n_s^{\mathrm{surf}} N^{-1/3} + n_s^{\mathrm{curv}} N^{-2/3}$.

Confinement of s electrons into the finite dot volume gives rise to the well-known gross-shell structure of ρ_s (cf. [17])

$$\rho_s(\epsilon) = \rho_s^{\mathrm{sm}}(\epsilon) + \rho_s^{\mathrm{sc}}(\epsilon) \tag{2}$$

with a smooth $\rho_s^{\mathrm{sm}}(\epsilon)$ and an oscillating $\rho_s^{\mathrm{sc}}(\epsilon)$ (i.e., shell correction) part, and an energy ϵ which we will measure from the bottom of the sp band ϵ_s. For instance, in the case of a 3D-shaped dot with a harmonic oscillator (HO) confining potential $[V(r) = m\omega^2 r^2/2 - \hbar\omega/2]$ and a uniform self-field H, both contributions can be expressed

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as [17,18]

$$\rho_\omega^{\rm sm}(\epsilon) = \frac{\epsilon(\epsilon + \hbar\omega)}{2(\hbar\omega)^3},$$
$$\rho_\omega^{\rm sc}(\epsilon) = \frac{\epsilon(\epsilon + \hbar\omega)}{(\hbar\omega)^3} \times \sum_{k=1} \cos\left(k\,\frac{2\pi\epsilon}{\omega}\right) j_0\left(\eta k\,\frac{2\pi\epsilon}{\omega}\right) q_k\,. \quad (3)$$

The Larmor frequency $\omega_L = eH/2mc$ satisfies the condition $\eta = \omega_L/\omega \ll 1$, j_0 is the spherical Bessel function, and the factor q_k measures the stability of a trajectory (cf., e.g., [19]); it permits a smooth truncation of the contribution from longer periodic orbits and can be chosen on the basis of the mean-free path l or the conductivity properties of the material as $q_k \approx q^k$ with $q \sim \exp\{-L/l\}$, where L measures the length of the primitive orbit (cf. also [17]).

Because of the shell structure, δn_s oscillates with varying cluster size. Using the abbreviations $\Delta_\uparrow = \epsilon_F - \epsilon_\uparrow$, $\Delta_\downarrow = \epsilon_\downarrow - \epsilon_F$, and $\Delta_s = \epsilon_F - \epsilon_s$, we can approximate the oscillating part of Eq. (1) by

$$\delta n_s^{\rm sc} \approx \frac{\Delta_\uparrow(1 + X_s)R}{N(\hbar\omega_s)4\pi\eta} \times \left[\arctan\left(\frac{q\sin(x)}{1 - q\cos(x)}\right)\right]_{x=2\pi(1-\eta)X_s}^{x=2\pi(1+\eta)X_s}, \quad (4)$$

where $R = y/\sinh(y)$ with $y = 2\pi k_B T/(\hbar\omega_s)$, and the quantity $X_s = (3n_s^0 N)^{1/3}$ counts the number of filled shells. Generally, $\Delta_\uparrow$ can be assumed to be small as compared to $\hbar\omega_s = \Delta_s/X_s$ which represents a convenient choice of the HO frequency [17].

Using the known properties of Ni and Co bulk material (cf. [8,16]) we can now calculate the size dependence of the cluster magnetic moment. The results are compared to experimental data in Fig. 1. Evidently, the shell model based on the band structure properties of *strong* ferromagnetic materials provides a realistic description of the magnetism of transition metal dots. The magnetic self-field smears out the magnetic moment oscillations especially for the large dots; this feature is seen to be essential for a good fit to the experimental data.

This electronic structure will be modified due to exchange coupling when the dots are arranged in sufficiently dense packing. For instance, if ferromagnets are separated by a nonmagnetic insulator the tunnel exchange spin current results in Anderson-type superexchange coupling, nonoscillatory with separation distance [8,20,21]. A similar coupling can be expected in a regular dot array with a coherent state of the dot supermoments. Too strong variations in the array geometry (e.g., variation of the dot sizes, or of the distances between the dots) will prevent the formation of a coherent state. Limiting conditions can be expressed within Anderson localization theory (see, for example, [22], and references therein) as $\Gamma/B < 2$, with Γ the level broadening due to variations, and B the miniband splitting. For sufficiently small Γ (cf. [9]), we obtain the zero temperature ($T = 0$) superexchange coupling constant J_0 as a difference of Nagaoka's state grand potential in the array (Ω_f) and in the uncoupled (Ω_d) dot system

$$J_0 = \Omega_f - \Omega_d \approx \int_{-\infty}^{\epsilon_F} d\epsilon\,(\epsilon_F - \epsilon)\,\delta\rho^c(\epsilon)\,; \quad (5)$$

D-dimensional periodic ordering of the interacting dots

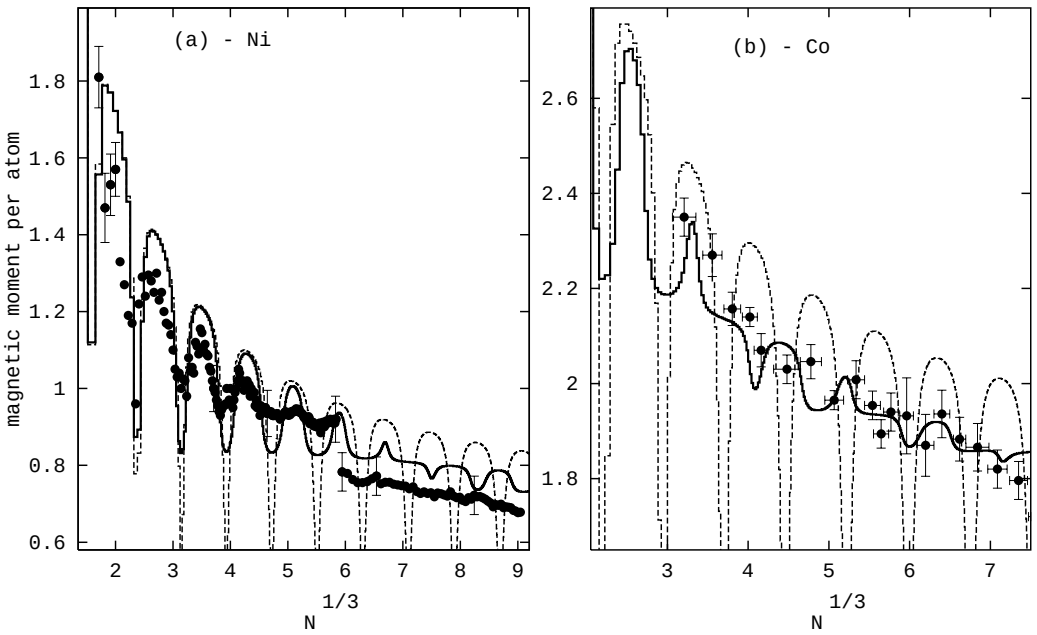

FIG. 1. Size dependence of the magnetic moment per atom (measured in μ_B) in (a) free Ni dots with $n_s^{\rm bulk} = 0.62$ and [bulk:surf:curv] = [1:3.1:1.0]; (b) free Co dots with $n_s^{\rm bulk} = 0.7$ and [bulk:surf:curv] = [1:3.1:2.1]. The solid lines display the results of the present calculations with a self-field $H = 0.7$ T (a) and $H = 1.9$ T (b). The dashed lines correspond to zero self-field. The dots show the experimental data of [11] (a) and [10] (b).

gives rise to a miniband structure $\Delta\epsilon(\mathbf{k})$ of active electrons with quasimomentum $\mathbf{k}$, causing a level density change

$$\delta\rho^c \approx \int \prod_{i=1}^{D} d\left(\frac{k_i a_i}{2\pi}\right)[\rho(\epsilon - \Delta\epsilon(\mathbf{k})) - \rho(\epsilon)] \quad (6)$$

with $a_i = a$ the period in the ith direction.

For dots separated by nonmagnetic tunnel barriers of sufficiently large heights $U_i = U$ and widths $b_i = b$ only the levels in the vicinity of the Fermi energy will give a noticeable contribution to the integral in Eq. (5). Neglecting the influence of the filled majority spin band at these energies, the miniband width B_e for the sp ($e = s$) and the minority spin d ($e = \downarrow$) electronic levels of energy ϵ is evaluated to leading order in $\hbar$ as [23]

$$B_e \approx 2\hbar\omega_e \exp\{-\xi\kappa b/\hbar\}, \quad (7)$$

where $\kappa = \sqrt{2m^*(U - \epsilon)}$ with m^* the electron effective mass in the barrier substrate. The parameter ξ ($\approx$1.7–2) depends on the shape of the barrier, and ω_e denotes the HO frequencies corresponding to s ($\omega_{e=s}$) and minority spin d [$\hbar\omega_{e=\downarrow} = \Delta_\downarrow(3n_h^0 N)^{-1/3}$] electrons. The exponential factor in Eq. (7) provides a measure for the overlap integral of the supermoment wave functions of two neighboring dots. Since such an overlap in the coupling region is small (see below), the dot wave functions are practically not distorted. Therefore, a cosine shape gives a good approximation for the miniband structure. Then the coupling constant Eq. (5) is further reduced, yielding for a two-dimensional array

$$J_0 \approx J_D J_B \quad (8)$$

with the components

$$J_D = (\epsilon_F - U)\hbar[\rho'_{\omega_s}(\Delta_s)\omega_s + \rho'_{\omega_\downarrow}(\Delta_\downarrow)\omega_\downarrow] \quad (9)$$

determined by the dot electronic structure, and

$$J_B = \frac{2\hbar^2}{m^*(\xi b)^2} \exp\{-\xi\kappa_F b/\hbar\}, \quad (10)$$

related to the barrier properties. Here $\kappa_F = \sqrt{2m^*(U - \epsilon_F)}$, and the *prime* denotes the energy derivative.

Equation (8) quantifies the Anderson-type superexchange coupling originating from tunneling between the superparamagnetic dots. The sign of the coupling constant is determined by the dot electronic structure and remains unchanged with interdot separation distance b, similarly to what is obtained for ferromagnetic layers abutted by an insulator [8,20,21]. The dot-size dependence contained in J_D is shown in Figs. 2 and 3 for Ni and Co systems, respectively. Since the number of minority spin holes and s electrons is equal in the case of nickel dots, the quantity J_D displays regular oscillations with varying dot diameter (see Fig. 2a). This is a consequence of the harmonic approximation giving a regular branching of levels into gross shells. The sign of J_D indicates a ferromagnetic type of superexchange when the gross shells are more than half filled, and it changes smoothly

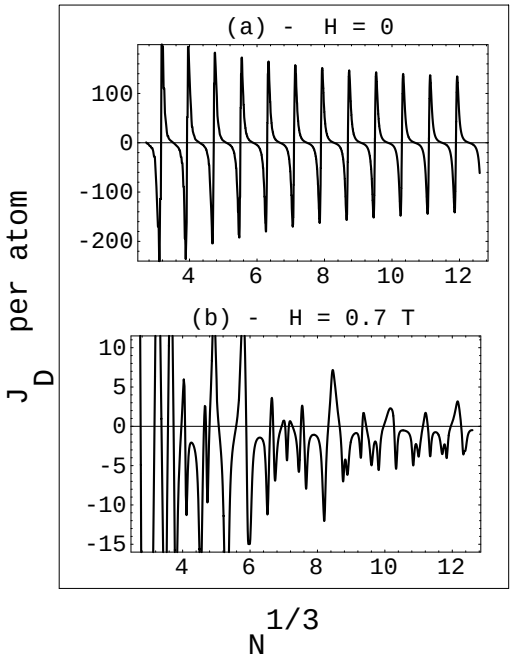

FIG. 2. The contribution J_D of the dot electronic structure to the superexchange interaction for a nickel dot array. (a) without self-field; (b) self-field ($H = 0.7$ T) included. $J_D > 0$ (< 0) leads to antiferro- (ferro-) magnetic coupling, respectively.

to an antiferromagnetic type for a gross-shell occupation below one-half. This behavior remains also if the self-field is taken into account in case of small dot diameters ($\sim$1 nm), while for larger sizes the exchange coupling of supermoments is preferredly ferromagnetic (Fig. 2). For the cobalt system the numbers of minority spin holes exceeds the number of s electrons. This leads to a beat structure in the size dependence of the coupling constant and to rather pronounced ferromagnetic ordering in case of larger sizes (see Fig. 3). Such a behavior is expected to be even more pronounced in an iron system because of the growing asymmetry in the number of minority spin holes and s electrons, respectively. We note, however, that the treatment of iron dots as an example of a *weak* ferromagnet should require special analysis.

The exponential decrease of J_B Eq. (10) arises from the exponentially decaying overlap of *superparamagnetic* dot wave functions extending their tail into the barrier. This restricts the interdot separation at which exchange can contribute to the magnetic ordering, in agreement with recent experiments (cf., e.g., [3]); in these studies, no long-range magnetic ordering was found in a system of self-organized Fe islands with too low surface coverage. With the cautious remark in mind made above about Fe dots, we may try to get a rough estimate for this system. The energy barrier can be approximated by $U - \epsilon_F \approx \varphi(b/b_0)U_F$ with $U_F \approx 4.5$–5 eV, and φ accounts for the proximity effect; it approaches *unity* at larger intercluster separations and *zero* at distances b corresponding to the substrate lattice constant. Assuming

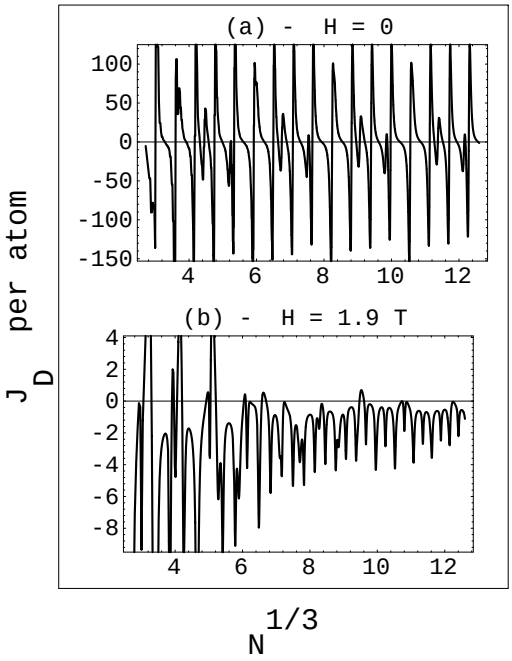

FIG. 3. The same as Fig. 2 for a cobalt dot array and $H = 1.9$ T.

$U - \epsilon_F \approx 3$ eV at $b \approx 1-1.5$ nm, Eq. (10) yields $J_B/\mu_B \approx 50-100$ G, which together with the factor J_D supports the estimate of Ref. [3] for the strength of the superexchange *magnetizing* field. We note that using a semiconductor substrate may allow for larger dot separations (lower tunnel barriers, smaller m^*) as compared to an insulator substrate; for example, in the case of carbon the barrier height could be reduced to ca. 1 eV (cf. [20]). Consequently, exponentially larger exchange fields can be obtained at the same interdot separations.

In summary, we have discussed magnetism in nanocrystals of strong ferromagnets and their arrays. It has been shown that the band-structure-based shell model provides a realistic description of the size-dependent magnetic properties of transition metal nanodots. In particular, this picture reproduces quite well the size dependence of the dot magnetic moment. Furthermore, the size dependence of the exchange coupling in arrays of strong ferromagnet nanodots has been analyzed for the first time. The band-structure-based shell model calculations yield magnetic ordering which oscillates between ferromagnetism and antiferromagnetism with increasing dot sizes. The calculations also show the importance of the self-magnetization of the dots giving rise to a preferential ferromagnetic type of supermoment exchange. It is worth noticing that dot structures with *zero* total flux of self-field are in practice restricted to a vortex or quasivortex (e.g., two domain) stable magnetic configurations. Such properties are found, e.g., for a *perfectly* disk-shaped ferromagnet of tens or hundreds of nm in diameter [24].

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