Theory of Tunneling Spectroscopy in Ferromagnetic Nanoparticles

C. M. Canali[1] and A. H. MacDonald[2]

[1]*Division of Solid State Theory, Department of Physics, Lund University, SE-223 62 Lund, Sweden*
[2]*Department of Physics, Indiana University, Bloomington, Indiana 47405*

(Received 31 July 2000)

We present a theory of the low-energy excitations of a ferromagnetic metal nanoparticle. In addition to the particle-hole excitations, which occur in a paramagnetic metal nanoparticle, we predict a branch of excitations involving the magnetization-orientation collective coordinate. Tunneling matrix elements are in general sizable for several different collective states associated with the same band configuration. We point out that the average change in ground state spin per added electron differs from noninteracting quasiparticle expectations, and that the change in the spin polarization, due to Zeeman coupling, is strongly influenced by Coulomb blockade physics.

PACS numbers: 73.40.Gk, 73.20.Dx, 73.23.Hk, 75.60.–d

The energies of many-particle states in metallic nanoparticles and semiconductor quantum dots can be measured directly by tracking the dependence of resonant tunneling conductance peaks on gate and bias voltages [1]. This technique has been used to study the interaction physics of quantum dots at weak fields [2] and in the quantum Hall regime [3], and metallic nanoparticles in both superconducting [4] and normal [5] states. In zero-field semiconductor quantum dots at high densities and in normal metallic nanoparticles, experiments are generally consistent with a model which acknowledges electron-electron interactions only in a mean-field electrostatic term that, because of its long range, gives rise to the Coulomb blockade effect [6]. The success of this simple interpretation is a consequence of the Fermi-liquid character of these interacting electron systems.

The present work is motivated by recent experimental studies [7] of tunneling via discrete energy levels in ferromagnetic cobalt nanoparticles that find resonance spacings smaller than predicted in an independent particle picture, and a dependence on external field qualitatively different from those in paramagnetic metal nanoparticles. Since bulk ferromagnetic metals have low-energy spin-wave excitations in addition to their Fermi liquid particle-hole excitations, it is natural, as suggested [7] by Guéron *et al.,* to seek an explanation in terms of the collective quantum physics of the magnetic order parameter field. In this Letter we address the interplay of quasiparticle and collective order parameter excitations in tunneling spectroscopy studies of ferromagnetic nanoparticles. Our conclusions are based in part on the properties of a simple exactly solvable toy model, described in the following paragraphs. We conclude that only states in which all singly occupied nanoparticle orbitals have aligned spins are relevant at low energies in ferromagnetic nanoparticles, and use this observation to derive expressions for the tunneling amplitudes of ground and excited many-particle collective spin states. Near fields where magnetization reversal occurs, many of these low-energy spin states have large tunneling amplitudes, and contribute significantly to the tunneling spectrum, partly explaining the enhanced density of resonances seen in experiment.

In ferromagnetic metals, short-range exchange interactions favor spin alignment, giving rise to an approximately rigid spin splitting of quasiparticle energies in the ferromagnetic ground state. Our toy model reflects this rigidity by assuming identical exchange constants between all pairs of orbitals:

$$\mathcal{H} = \sum_{j,\sigma} c^{\dagger}_{j,\sigma} c_{j,\sigma} \epsilon_j - \frac{U}{8} \times \sum_{j,k} \sum_{s,s',t,t'} c^{\dagger}_{j,s'} \vec{\tau}_{s',s} c_{j,s} \cdot c^{\dagger}_{k,t'} \vec{\tau}_{t',t} c_{k,t} \,. \quad (1)$$

In Eq. (1) ϵ_j is a nanoparticle orbital energy that incorporates the charge correlation physics neglected in our model Hamiltonian and $\vec{\tau}$ is the Pauli spin matrix vector. The single-particle orbitals have an average spacing inversely proportional to the volume of the nanoparticle and are expected to exhibit spectral rigidity [8]. The many-particle spectrum of this Hamiltonian follows readily from the following observations: (i) the total occupation of each orbital is a good quantum number; (ii) the interaction term is proportional to the square of the total electron spin operator $\vec{S}_{\rm tot}$. The 2^{N_s} states with a given set of N_s singly occupied orbitals have their band energy degeneracy lifted by the interaction energy $-(U/2)S_{\rm tot}(S_{\rm tot} + 1)$, where the total spin $S_{\rm tot}$ has a maximum value $N_s/2$. We show below that only this $(N_s + 1)$-fold degenerate spin multiplet is relevant to the low-energy physics of a ferromagnetic nanoparticle.

We start by considering the ground state of a ferromagnetic metal nanoparticle in which majority and minority spin quasiparticles are occupied up to their Fermi energies. We take these to have the values ϵ_{Fa} and ϵ_{Fi} in the absence of an external magnetic field at a reference total particle number. We are interested in how the nanoparticle evolves as a function of external field and gate voltage. We assume, for simplicity, that the quasiparticle energy levels

of majority and minority spins are equally spaced near their respective Fermi energies. It follows from the considerations of the previous paragraph that the total energy, relative to that of the reference state, is

$$\delta E = [\epsilon_{Fa} - \Delta/2 + \delta_a/2]\delta N_a + [\epsilon_{Fi} + \Delta/2 + \delta_i/2]\delta N_i + E_{cb}(\delta N_a + \delta N_i)^2/2 + \frac{\delta N_a^2}{2}[\delta_a - \Delta/2(2S_0 + 1)] + \frac{\delta N_i^2}{2}[\delta_i - \Delta/2(2S_0 + 1)] + \delta N_a \delta N_i \frac{\Delta}{2(2S_0 + 1)} - (V_g + g\mu_B B/2)\delta N_a - (V_g - g\mu_B B/2)\delta N_i . \quad (2)$$

In this energy expression, $\delta_{a,i}$ are level spacings, and we have added by hand the electrostatic Coulomb blockade term, which depends only on the total number of particles in the grain. The terms proportional to Δ in Eq. (2) originate from the interaction energy $-US_{\rm tot}(S_{\rm tot} + 1)/2$; the notational change $U \to \Delta/(2S_0 + 1)$ is motivated by the identification, explained below, of Δ as the spin-splitting energy of the quasiparticle bands. Here $S_0 = (N_{a0} - N_{i0})/2$ is the ground state total spin of the reference state and $S_{\rm tot} = S_0 + (\delta N_a - \delta N_i)/2$. Note that for a ferromagnetic particle S_0 will be proportional to volume. We have not explicitly indicated the capacitance ratio relating the gate voltage and the chemical potential of the nanoparticle, and have assumed that only Zeeman coupling to an external field is important.

Stability of the reference system ground state requires that its energy increases at fixed total particle number N both for $S_{\rm tot} \to S_0 + 1$ ($\delta N_a = 1, \delta N_i = -1$) and $S_{\rm tot} \to S_0 - 1$ ($\delta N_a = -1, \delta N_i = +1$). From this it follows that

$$|\epsilon_{Fa} - \epsilon_{Fi} - \Delta + (\delta_a - \delta_i)/2| < [\delta_a + \delta_i - 2\Delta/(2S_0 + 1)]. \quad (3)$$

Since the right-hand side of Eq. (3) $\sim N_A^{-1}$, where N_A is the number of atoms in the grain, it follows that $\Delta = \epsilon_{Fa} - \epsilon_{Fi}$ to within a fluctuating mesoscopic correction, i.e., that Δ is the quasiparticle spin splitting. The energy difference between the $S_{\rm tot} = (N_a - N_i)/2$ states retained in our considerations and the $S_{\rm tot} \le (N_a - N_i)/2 - 1$ states we have discarded is $\Delta 2S_0/(2S_0 + 1) \sim \Delta$, well outside the energy range of interest [9].

It is instructive to minimize the energy by considering N_a and N_i as continuous variables, thereby obtaining the trend lines around which the mesoscopic ground state spin and charge quantum numbers fluctuate as gate voltage and external field vary. We find that

$$\begin{aligned} C_{aa}^{-1}\delta N_a + C_{ai}^{-1}\delta N_i &= V_g + g\mu_B B , \\ C_{ia}^{-1}\delta N_a + C_{ii}^{-1}\delta N_i &= V_g - g\mu_B B , \end{aligned} \quad (4)$$

where

$$\begin{aligned} C_{aa}^{-1} &= E_{cb} + \delta_a - \Delta/4S_0 , \\ C_{ai}^{-1} &= C_{ia}^{-1} = E_{cb} + \Delta/4S_0 , \\ C_{ii}^{-1} &= E_{cb} + \delta_i - \Delta/4S_0 . \end{aligned} \quad (5)$$

The inverse capacitance matrix C^{-1} describes the coupled spin and charge response of the nanoparticle. This coupling is responsible for the variation of total particle number with external field observed [10,11] by Ono *et al.*

Equation (4) can be solved to obtain the variation of both N_a and N_i with either V_g or B. For example, we find that

$$\frac{dS_{\rm tot}}{d(g\mu_B B)} = \frac{2E_{cb} + (\delta_a + \delta_i)/2}{E_{cb}(\delta_a + \delta_i - \Delta/S_0) + \delta_a\delta_i - \Delta(\delta_a + \delta_i)/4S_0} , \quad (6)$$

and that

$$\frac{dN_a/dV_g}{dN_i/dV_g} = \frac{M_{ii} - M_{ai}}{M_{aa} - M_{ai}} = \frac{\delta_i - \Delta/2S_0}{\delta_a - \Delta/2S_0} . \quad (7)$$

Level spacings and exchange splittings in metallic ferromagnet nanoparticles can be estimated from spin-density functional band structure calculations. For the case of cobalt particles [12] $\delta_a = 5.55$ eV$/N_A$, $\delta_i = 1.43$ eV$/N_A$, $2S_0 = 1.65N_A$, and $\Delta/2S_0 = 1.07$ eV$/N_A$. The Coulomb blockade energy is sensitive to the screening environment of the nanoparticle; for a grain with $N_A \approx 1500$, Guéron *et al.* [7] find that $E_{cb} \ge 30$ meV. As expected, the largest elements in the inverse capacitance matrix are the purely electrostatic Coulomb blockade contributions. Evaluating the right-hand side of Eq. (7) we find that $S_{\rm tot}$ almost always *decreases* when particles are added. The response of $S_{\rm tot}$ to external fields, given by Eq. (6), is smaller than would be expected naively, because E_{cb}, the dominant mesoscopic energy scale, suppresses charge fluctuations causing the larger (majority spin) level spacing to limit this response. Typically the relatively large value of E_{cb} suppresses the total charge response to both gate voltage and external field. For example, for $N_A = 1500$ and $E_{cb} = 30$ meV, typical for the particle size studied by Guéron *et al.* [7], we find that $\delta N_a = 0.0025dV_g + 0.306d(g\mu_B B)$ and $\delta N_i = 0.0302dV_g - 0.321d(g\mu_B B)$ with energies in meV.

In the model discussed so far, structure would appear in the bias dependence of the tunneling current only on the scale of the single-particle level spacing. Following Guéron *et al.* [7], we seek an explanation of experiment by invoking spin-orbit coupling and long-range dipole interactions between the electronic spins. In cobalt, the typical band energy shift due to spin-orbit coupling is [13] $\delta E \sim 1$ meV; the dependence of the total band energy on spin-moment orientation results from a partially canceling sum of spin-orbit energy shifts over all singly occupied orbitals. The typical spin-orbit matrix element between an

individual pair of orbitals in a grain is $\sim \delta E/N_A$, ~ 1 μeV for the grain sizes of interest to us. These considerations justify starting from a model which neglects spin-orbit coupling of states with different band configurations and uses the bulk magnetocrystalline anisotropy coefficient to describe its effect within a single multiplet:

$$\mathcal{H} = \mathcal{H} - K(S_z/S_0)^2, \tag{8}$$

where, for cobalt [14], $K \sim 0.073 N_A$ meV. Note for $N_A \sim 1500$, $K \sim 0.1$ eV, much larger than either level spacing or Coulomb blockade energy scales.

A theory of tunneling spectroscopy in ferromagnetic nanoparticles requires results for tunneling matrix elements between many-body eigenstates, found by diagonalizing the collective spin Hamiltonian

$$\mathcal{H} = E_{\text{band}} - K(S_z/S_0)^2 - g\mu_B \vec{B} \cdot \vec{S} \tag{9}$$

$$= E_{\text{band}} - K/S_0(S_z^2/S_0 + \alpha \hat{B} \cdot \vec{S}), \tag{10}$$

where $K/S_0 \approx 0.05$ meV is the natural energy scale and $\alpha \equiv g\mu_B B/(K/S_0) \sim 2B[\text{T}]$ is the (dimensionless) strength of the magnetic field. In Fig. 1 we plot the energy eigenvalues E_n as a function of the expectation value of S_z for the corresponding eigenstates $|S_0, n\rangle$ for $S_0 = 25$ and $\hat{B}$ oriented at $\theta_{\text{ext}} = \pi/4$ from the easy axis, $\hat{z}$.

The curves are offset for clarity, starting at the bottom with $\alpha = -2$. For large negative α the ground state spin is polarized along the field direction, and gradually reorients toward $-\hat{z}$ as the field is ramped to zero. At $\alpha = 0$ a level crossing occurs and the ground state is now polarized along $\hat{z}$. The former ground state, now classically metastable and separated from the true ground state by a potential barrier, is apparent in the spectrum until the classical switching field is reached at $\alpha_{SW} \sim +1.2$. The classical down-sweep metastable states appear at negative values of α and positive values of $\langle S_0, n|S_z|S_0, n\rangle$.

In order to evaluate the many-particle tunneling matrix elements, we express these eigenstates in terms of microscopic electronic degrees of freedom. For a given set of quasiparticle occupations, the microscopic state for collective spins oriented in direction $\hat{\Omega} = \hat{\Omega}(\theta, \phi)$ is

$$|\Psi(\hat{\Omega})\rangle = \prod_{j \in S} [\mathcal{V}_\uparrow(\hat{\Omega}) c_{j,\uparrow}^\dagger + \mathcal{V}_\downarrow(\hat{\Omega}) c_{j,\downarrow}^\dagger] \prod_{k \in D} c_{k,\uparrow}^\dagger c_{k,\downarrow}^\dagger |0\rangle, \tag{11}$$

where D and S are the sets of doubly and singly occupied orbitals, respectively; $\mathcal{V}_\uparrow(\hat{\Omega}) = \cos(\theta/2)\exp(i\phi)$ and $\mathcal{V}_\downarrow(\hat{\Omega}) = \sin(\theta/2)\exp(-i\phi)$.

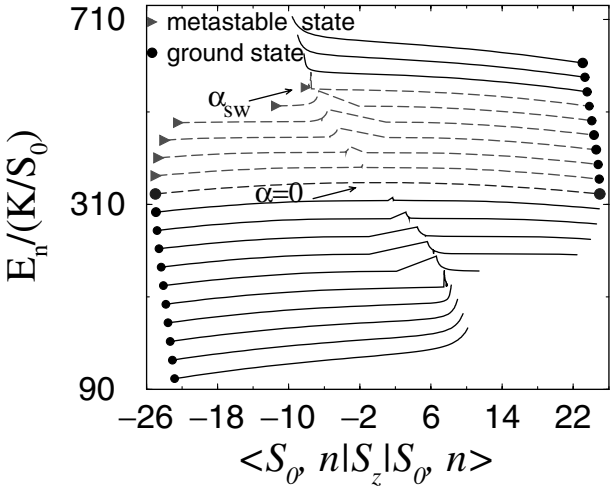

FIG. 1. Energy eigenvalues E_n vs $\langle S_0, n|S_z|S_0, n\rangle$ for the collective spin Hamiltonian. The curves, offset for clarity, correspond to increasing values of α, starting from $\alpha = -2$ at the bottom. Here $S_0 = 25$ and $\hat{B}$ is oriented at $\pi/4$ from the easy axis, $\hat{z}$. At $\alpha = \alpha_{\text{sw}} \sim 1.2$, the metastable state disappears.

The matrix element between states with collective spin orientations $\hat{\Omega}'$ and $\hat{\Omega}$ for adding an electron with spin orientation $\hat{\Omega}_{\text{ext}}$ to an empty orbital, thereby increasing N_s and S_{tot}, is

$$\langle \Psi(\hat{\Omega}')|c^\dagger(\hat{\Omega}_{\text{ext}})|\Psi(\hat{\Omega})\rangle_+ = \langle \hat{\Omega}' \,|\, \hat{\Omega}\rangle_{1/2}^{N_s} \langle \hat{\Omega}' \,|\, \hat{\Omega}_{\text{ext}}\rangle_{1/2}, \tag{12}$$

where $\langle \hat{\Omega}' \,|\, \hat{\Omega}\rangle_{1/2}$ is the inner product of spin-1/2 coherent states [15].

Similarly the matrix element for adding an electron with spin orientation $-\hat{\Omega}_{\text{ext}}$ to a singly occupied orbital, thereby decreasing N_s and S_{tot} is

$$\langle \Psi(\hat{\Omega}')|c^\dagger(\hat{\Omega}_{\text{ext}})|\hat{\Psi}(\hat{\Omega})\rangle_- = \langle \hat{\Omega}' \,|\, \hat{\Omega}\rangle_{1/2}^{N_s - 1} \langle \hat{\Omega} \,|\, \hat{\Omega}_{\text{ext}}\rangle_{1/2}. \tag{13}$$

The tunneling spectral function is defined as

$$A_\pm(\omega) = \sum_n |\langle (N_s \pm 1)/2, n|c^\dagger(\hat{\Omega}_{\text{ext}})\,|N_s/2, 0\rangle|^2 \times \delta[\omega - (E_{(N_s \pm 1)/2, n} - E_{N_s/2,0})], \tag{14}$$

where $|(N_s \pm 1)/2, n\rangle$, $E_{(N_s \pm 1)/2, n}$ are collective spin eigenstates and eigenvalues of $\mathcal{H}$ in the $S_{\text{tot}} = S_0 \pm 1/2 = (N_s \pm 1)/2$ manifold, respectively. To evaluate the matrix elements in Eq. (14), we expand these eigenstates first in terms of eigenstates of S_z and then in terms of spin-coherent states [15] with a definite $\hat{\Omega}$. Using Eqs. (12) and (13), we finally arrive at the simplified expressions

$$\langle (N_s \pm 1)/2, n|c^\dagger(\hat{\Omega}_{\text{ext}})\,|N_s/2, 0\rangle = \sum_\sigma \sum_{m'} \sum_m \mathcal{V}_\sigma(\hat{\Omega}_{\text{ext}}) c_n^{m'}(N_s + 1) c_0^m(N_s) \left\langle \frac{N_s \pm 1}{2}\, m' \middle| \frac{N_s}{2}\, m; \frac{1}{2}\, \sigma \right\rangle, \tag{15}$$

where $c_n^m(N_s)$ are the expansion coefficients of $|N_s/2, n\rangle$; $\langle \frac{N_s \pm 1}{2} m' \,|\, \frac{N_s}{2} m; \frac{1}{2}\sigma\rangle$ are Clebsch-Gordan coefficients for adding the angular momenta $S_0 = N_s/2$ and $s = 1/2$.

Many-particle tunneling spectra for $S_0 = N_s/2 = 25$ and $\theta_{\text{ext}} = \pi/4$ are illustrated in Fig. 2: In these "up-sweep" calculations, we chose $|N_s/2, 0\rangle$ to be the true ground state for $\alpha < 0$ and $\alpha > \alpha_{\text{sw}}$. In the field interval $0 < \alpha < \alpha_{\text{sw}}$, however, we allowed the system to be initially in the metastable stable, discussed in Fig. 1. These figures clearly show that the tunneling spectra have

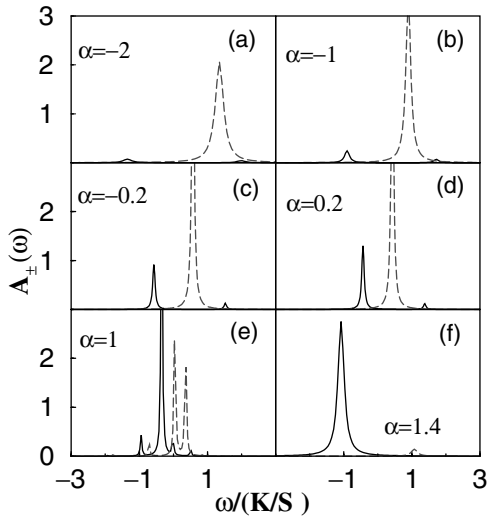

FIG. 2. The tunneling spectral function for the collective spin model, at different values of the magnetic field, specified by α. The solid and dashed lines refer to the $S_{\rm tot} \rightarrow S_0 \pm 1$ transitions, respectively. $S_0 = 25$ and $\hat{B}$ is oriented at $\pi/4$ from the easy axis $\hat{z}$. For $0 < \alpha < \alpha_{\rm sw} \sim 1.2$, the system is in a metastable state (see Fig. 1), before the tunneling takes place. In (e), α is near $\alpha_{\rm sw}$, where the metastable state disappears and the magnetization reversal occurs.

a regime near the classical switching field, where many excited states contribute, giving rise to a dense tunneling spectrum, like that seen in experiment.

For a particular ferromagnetic metal particle at a given gate voltage, the onset tunneling spectra can be dominated by an intermediate state with either increased or decreased particle number. In either case, the lowest energy multiplet could have $S_{\rm tot} = S_0 \pm 1/2$, although decreases will be more common for particle addition and increases for particle removal, as we have discussed. The calculations presented here can explain a dense tunneling spectra with level spacing $\sim K/S_0$ rather than δ near the classical switching field, but not at general fields. The magnetic anisotropy energy landscape of a realistic nanoparticle is certain to be more complex than in our model calculation. There is clearly a shape anisotropy, since the particles used in the experiment are approximately hemispherical. A self-consistent calculation [16] on small, irregularly shaped clusters predicts a magnetic anisotropy energy that can be much larger than the one we have used here. If this were the case, this energy scale would no longer be a candidate for explaining the experiment. Note, however, that for ellipsoidal particles, the shape anisotropy constant is comparable to the bulk constant [14]. On the other hand, magnetostatic interactions with nearby particles and more subtle surface effects [17] are probably important but much harder to estimate. Finally, nonequilibrium effects [7,18] and spin-orbit coupling between different band multiplets could also contribute significantly to the ubiquity of dense tunneling spectra observed in experiment.

We are grateful to M. Deshmukh, S. Guéron, D. Ralph, and J. von Delft for helpful interactions. C. M. C. thanks the Centre for Advanced Study in Oslo, Norway, for hospitality. A. H. M. was supported by the National Science Foundation under Grant No. DMR-9714055.

[1] M. A. Kastner, Rev. Mod. Phys. **64**, 849 (1992); Phys. Today **46**, No. 1, 24 (1993), and references therein.
[2] A. M. Chang *et al.,* Phys. Rev. Lett. **76**, 1695 (1996); J. A. Folk *et al.,* Phys. Rev. Lett. **76**, 1699 (1996); S. Tarucha *et al.,* Phys. Rev. Lett. **77**, 3613 (1996).
[3] R. C. Ashoori, Nature (London) **379**, 413 (1996).
[4] C. T. Black, D. C. Ralph, and M. Tinkham, Phys. Rev. Lett. **76**, 688 (1996); **78**, 4087 (1997).
[5] D. C. Ralph *et al.,* Phys. Rev. Lett. **74**, 3241 (1995); Physica (Amsterdam) **218B**, 258 (1996); D. Davidovic and M. Tinkham, Phys. Rev. Lett. **83**, 1644 (1999).
[6] For reviews see D. V. Averin and K. K. Likharev, in *Mesoscopic Phenomena in Solids,* edited by B. A. Altschuler, P. A. Lee, and R. A. Webb (Elsevier, Amsterdam, 1991); G.-L. Ingold and Yu. V. Nazarov, in *Single Charge Tunneling,* edited by H. Grabert and M. H. Devoret, NATO Advanced Study Institutes, Ser. B, Vol. 294 (Plenum, New York, 1992).
[7] S. Guéron, M. M. Deshmukh, E. B. Myers, and D. C. Ralph, Phys. Rev. Lett. **83**, 4148 (1999); M. M. Deshmukh, S. Guéron, E. B. Myers, A. N. Pasupathy, J. R. Petta, and D. C. Ralph, Bull. Am. Phys. Soc. **45**, 525 (2000).
[8] K. B. Efetov, Adv. Phys. **32**, 53 (1983); *Supersymmetry in Disorder and Chaos* (Cambridge University Press, Cambridge, 1997).
[9] In the bulk, the toy model we are using has a collective spin-wave spectrum with a gap $\sim\Delta$. In a more realistic model the spin-wave spectrum would be gapless without spin-orbit interactions. In such a model, the energy scale on which $S < N_s/2$ states would become important equals the spin-wave energy at a wavelength comparable to the particle dimension. However, this much smaller scale is still safely outside the range of interest to us.
[10] K. Ono, H. Shimada, and Y. Ootuka, J. Phys. Soc. Jpn. **66**, 1261 (1997); **67**, 2852 (1998).
[11] A. H. MacDonald, in *Statistical and Dynamical Aspects of Mesoscopic Systems,* Lecture Notes in Physics, edited by D. Reguera, G. Platero, L. L. Bonilla, and J. M. Rubi (Springer, Berlin, 2000).
[12] Values for majority and minority spin densities of states per atom ($\mathcal{D}_{a,i}$), band splittings, and majority and minority spin densities per atom ($\mathcal{N}_{a,i}$) for ferromagnetic elements are listed by D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986). $\delta_{a,i}\mathcal{D}_{a,i}N_A = 1$, $2S_0/N_A = \mathcal{N}_a - \mathcal{N}_i$.
[13] D. D. Koelling and A. H. MacDonald, in *Relativistic Effects in Metals,* NATO ASI, Ser. B, Vol. 87 (Plenum, New York, 1983), p. 227.
[14] R. Skomski and J. M. D. Coey, *Permanent Magnetism* (Institute of Physics, Bristol, 1999).
[15] Assa Auerbach, *Interacting Electrons and Quantum Magnetism* (Springer-Verlag, New York, 1994).
[16] G. M. Pastor *et al.,* Phys. Rev. Lett. **75**, 326 (1995).
[17] R. H. Kodama *et al.,* Phys. Rev. Lett. **79**, 1393 (1997).
[18] O. Agam, N. S. Wingreen, B. L. Altshuler, D. C. Ralph, and M. Tinkham, Phys. Rev. Lett. **78**, 1956 (1997).