Enhancement of the Curie temperature in small particles of weak itinerant ferromagnets

L. Peters, M. I. Katsnelson, and A. Kirilyuk
Radboud University Nijmegen, Institute for Molecules and Materials, NL-6525 AJ Nijmegen, The Netherlands
(Dated: June 2, 2011)

Self consistent renormalization theory of itinerant ferromagnets is used to calculate the Curie temperature of clusters down to approximately 100 atoms in size. In these clusters the electrons responsible for the magnetic properties are assumed to be (weakly) itinerant. It is shown that the Curie temperature can be larger than in the bulk. The effect originates from the phenomenon of level repulsion in chaotic quantum systems, which suppresses spin fluctuations. Since the latter destroy the magnetic order the resulting Curie temperature increases, contrary to expectations of the naïve Stoner picture. The calculations are done assuming that the energy levels of the cluster are described by the Gaussian Orthogonal Ensemble of random matrix theory.

I. INTRODUCTION

Nowadays, nanotechnology is one of the most promising research areas. By using atoms and molecules as building blocks or by down scaling macroscopic objects, a large variety of nano-scale objects can be created. These nano-scale objects possess interesting physical properties substantially differing from the bulk [1]. It is size quantization of energy levels that could cause, sometimes, a dramatic difference of optical, electronic or chemical properties compared to the bulk. Applications in material science, health care, etc. are offered for these nano-objects [2].

Studying clusters containing tens to tens of thousands of atoms is a subject of special interest [3]. Such small particles demonstrate unusual mechanical, optical, and magnetic properties and chemical activity. The latter is crucial, for example, for their use in catalysis processes. However, the precise mechanisms behind the physical and chemical properties of the clusters are not yet fully understood [1]. For new applications and improvements of existing ones it is extremely important to understand these physical principles.

The study of magnetic properties is one of the methods to gather information about the cluster's behavior. Namely, the magnetic properties are sensitive to atomic and electronic structure, quantum size effects, surface to volume ratio, and symmetry. Several experiments demonstrate unusual magnetism of metallic clusters. For example, it was found that the clusters of 3d transition metals iron, cobalt and nickel, show enhanced ferromagnetism in comparison with the bulk [4–6]. Further, rhodium clusters appeared to become ferromagnetic while in the bulk rhodium is paramagnet [7]. For manganese, a change of magnetic order from ferro- to antiferromagnetism occurs during the transition from cluster to the bulk regime [8].

In general it is a complicated matter to understand the physical principles behind the magnetic properties of metallic clusters. Within the picture of localized magnetic moments described by the Heisenberg model one could expect that the smaller the cluster size and, thus, the larger the ratio surface to bulk, the weaker the magnetism is, due to a lower coordination of surface atoms. For an itinerant electron system the influence of downscaling is not immediately clear. For certain small cluster sizes so called shell effects give rise to an increased density of states near the Fermi level [9] and thus, due to the Stoner criterion [10], an increased tendency towards ferromagnetism. Besides an influence on the density of states, the size could also have an effect on the thermal spin fluctuations responsible for the reduction of magnetic order, whose role is crucial for the understanding of the magnetic properties at finite temperatures [10].

Note that in ultra thin films finite size effects also cause interesting physical features such as changes in the Curie temperature [11, 12]. For example in Gd ultra thin films an increased surface Curie temperature is observed compared to the bulk [11].

The theory of itinerant electron magnetism is, in general, very complicated and still controversial (for a review of some modern approaches, see Refs. 13, 14 and references therein). For a special case of weak itinerant ferromagnets close enough to the point of the Stoner instability a very successful self consistent renormalization (SCR) theory has been developed [10, 15]. This theory clarifies the role of spin fluctuations in finite-temperature magnetism and allows us to calculate the Curie temperature. Here we use this theory to study the size effects on the Curie temperature for metallic clusters, down to approximately 100 atoms in size. It appears that suppression of the spin fluctuations leads to an increase of the Curie temperature when going to smaller cluster sizes.

II. THE SELF CONSISTENT RENORMALIZATION THEORY OF WEAK ITINERANT FERROMAGNETISM

For a convenience of readers, we present in this section a brief overview of the SCR theory, following Ref. 10. We deal with the simplest model of itinerant electron magnetism, that is, the Hubbard model with the

Hamiltonian

$$H = \sum_{j,l}\sum_{\sigma} t_{jl} c^{\dagger}_{j\sigma} c_{l\sigma} + U \sum_{j} n_{j\uparrow} n_{j\downarrow}$$
$$= \sum_{k}\sum_{\sigma} \epsilon(k) a^{\dagger}_{k\sigma} a_{k\sigma} + I \sum_{q}\sum_{k}\sum_{k'} a^{\dagger}_{k+q\uparrow} a^{\dagger}_{k'-q\downarrow} a_{k'\downarrow} a_{k\uparrow}. \quad (1)$$

Here t_{jl} is the transfer integral between the Wannier orbitals at sites j and l, $\epsilon(k)$ is its Fourier transform, that is, the band energy dependent of the wave vector k, $a_{k\sigma}$ is the annihilation operator for the Bloch state, $c_{l\sigma}$ is the annihilation operator for the Wannier state, $n_{j\uparrow}$ is the occupation number operator for the Wannier state at site j with spin-up, U is the Coulomb interaction energy between two electrons on the same site and $I = \frac{U}{N_0}$ with N_0 the total number of atoms. Thus, the first term of the Hubbard model is the hopping term or tight-binding model and the second term is the on-site Coulomb interaction term.

The simplest way to approximate the interaction term is by using the Hartree-Fock approximation, which leads to the familiar Stoner theory:

$$n_{j\uparrow} n_{j\downarrow} \xrightarrow{HFA} n_{j\uparrow}\langle n_{j\downarrow}\rangle + n_{j\downarrow}\langle n_{j\uparrow}\rangle - \langle n_{j\uparrow}\rangle\langle n_{j\downarrow}\rangle. \quad (2)$$

Here the $\langle \ldots \rangle$ denotes the statistical average of the quantity inside the brackets. For the case of a ferromagnet, the statistical average of the occupation number is supposed to be site-independent: $\langle n_{j\uparrow}\rangle = \langle n_{\uparrow}\rangle = n_{\uparrow}$. Using the approximation of (2) for Eq. (1) and by rewriting this expression, leads to

$$H = \sum_{k}\sum_{\sigma} E_{k\sigma} a^{\dagger}_{k\sigma} a_{k\sigma} + \frac{1}{4} I N^2 - I M^2. \quad (3)$$

Here N is the total number of electrons, M is the magnetization and $E_{k\sigma}$ is the single electron energy given by

$$\begin{aligned} E_{k\sigma} &= \epsilon_k + \sigma\Delta, \\ \Delta &= IM + \mu_B \tilde{H} \end{aligned} \quad (4)$$

with σ equal to 1 for spin-up and to -1 for spin down, μ_B the Bohr magneton and $\tilde{H}$ an external magnetic field. Further, 2Δ is the band splitting between the spin-up and spin-down bands. This ferromagnetic state is stable at temperature $T = 0$ if $I\rho(E_F) > 1$ (Stoner criterion) with $\rho(E_F)$ the density of states (per whole system per spin) at the Fermi level.

From the results of Eqs. (3) and (4) it is possible to derive the thermodynamic properties of the system in the Stoner theory [10]. The Curie temperature, which is of main interest here, can be calculated from the divergence of the static magnetic susceptibility of the system, which within the Stoner theory is given by

$$\chi(T) = \frac{\chi_0(T)}{1 - I\chi_0(T)}. \quad (5)$$

Here χ_0 is the static magnetic susceptibility of a non-interacting system (i.e. with $I = 0$). For the bulk χ_0 is given by

$$\chi_0(T) = \rho(E_F)\left[1 - \frac{\pi^2}{6} R T^2 + \ldots\right]. \quad (6)$$

with $R = \left(\frac{\rho'}{\rho}\right)^2 - \left(\frac{\rho''}{\rho}\right)\Big|_{E=E_F}$ and the accent corresponds to the derivative to E.

Thus, from Eq. (5) and the divergence of the static magnetic susceptibility the Curie temperature T_C follows from

$$1 - I\chi_0(T_C) = 0. \quad (7)$$

For the case of weak itinerant ferromagnets when

$$0 < I\rho(E_F) - 1 \ll 1. \quad (8)$$

the Stoner Curie temperature (7) is estimated as

$$T_C^S \propto E_F \sqrt{I\rho(E_F) - 1}. \quad (9)$$

It is well known that Curie temperatures predicted from this equation are too high compared to the experimental data [10, 13]. The reason is a neglect of spin fluctuations that allow magnetic excitations at lower energy: it is easier to rotate the spins than to change their length like in the Stoner theory.

The SCR theory that takes spin fluctuations into account is formulated in the following way [10] (an alternative approach based on diagram technique has been developed in Ref. 13). The transverse dynamic magnetic susceptibility $\chi^{-+}(q,\omega)$ can be formally represented as

$$\chi^{-+}(q,\omega) = \frac{\chi_0^{-+}(q,\omega)}{1 - I\chi_0^{-+}(q,\omega) + \lambda_{MI}(q,\omega)}. \quad (10)$$

Here $\chi_0^{-+}(q,\omega)$ is the transverse dynamic magnetic susceptibility for non-interacting electrons with spin split bands, q is the wave-vector and ω the frequency. In general the problem is to find $\lambda_{MI}(q,\omega)$ of Eq. (10) to make the expression for the dynamic susceptibility exact. For this purpose the total free energy F of a system is expressed in terms of the exact transverse dynamic susceptibility using the Hellmann-Feynman theorem:

$$F = F_0 + \Delta F$$
$$= F_0 - \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \coth\left(\frac{\omega}{2T}\right) \sum_{q} \int_0^I dI \mathrm{Im}\left[\chi^{-+}(q,\omega)\right]. \quad (11)$$

Here F_0 is the free energy of a non-interacting system. Then, one can use the self consistency condition to find $\lambda_{MI}(q,\omega)$. This means that the static magnetic susceptibility calculated from the free energy of Eq. (11) (via $\frac{\partial^2 F}{\partial^2 M} = \frac{1}{\chi}$) is equal to the static long wave-length limit of

the exact transverse dynamic magnetic susceptibility of Eq. (10).

Of course, this condition is not enough to find the whole *function* λ. However, for the weak itinerant systems where the condition (8) is fulfilled one can assume that λ can be considered in Eq. (11) as a *number* independent on M, I, ω and q; a formal justification has been given in Ref. 15. As a result, λ is given by the expression [10]

$$\begin{aligned}\lambda(T,d) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \coth\left(\frac{\omega}{2T}\right) \mathrm{Im}\left\{G(\omega,d)\right\},\\ G(\omega,d) &= -\alpha\chi_0 \sum_q \left[\frac{f_M\left(\frac{\partial^2 f_M}{\partial^2 M}\right)}{d+1-f_M} + \frac{(d+1)\left(\frac{\partial f_M}{\partial M}\right)^2}{(d+1-f_M)^2}\right]_{M=0}.\end{aligned} \tag{12}$$

Here $\alpha = I\chi_0$, $f_M = \chi_0^{-+}(q,\omega)/\chi_0$, d is defined as $\chi_0/\chi \equiv \alpha d = 1-\alpha+\lambda(T,d)$ and $\chi_0 \equiv \chi_0^{-+}(0,0)$. At the Curie temperature $d=0$ and $M=0$, which makes it natural to expand f_M in terms of small ω and q ($\omega \ll E_F$ and $q \ll k_F$ respectively with k_F the Fermi wave-vector) and to approximate the nominators of Eq. (12) by their static and long wavelength limit. Thus, at the Curie temperature f_M can be approximated for the bulk by

$$f_0 = 1 - Aq^2 + iC\frac{\omega}{q}, \tag{13}$$

where A and C are constants (depending on the shape of the Fermi surface), and the subscript zero refers to $M=0$ [10].

By using the condition of divergence of the static magnetic susceptibility, the Curie temperature for a weak itinerant system is given by the equation

$$1 - I\chi_0(T_C) + \lambda(T_C,0) = 0. \tag{14}$$

Here, it can be noticed that it is actually λ which takes the influence of the spin density fluctuations on the Curie temperature into account. For further calculations it is convenient to separate λ in the following two parts:

$$\begin{aligned}&\lambda(T,0) = \lambda_0 + \lambda_1,\\ &\lambda_0 = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \mathrm{sign}\{\omega\}\mathrm{Im}\left\{G(\omega,0)\right\},\\ &\lambda_1 = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \mathrm{sign}\{\omega\}\frac{2}{e^{\frac{|\omega|}{T}}-1}\mathrm{Im}\left\{G(\omega,0)\right\}.\end{aligned} \tag{15}$$

The function λ_0 is the temperature independent part, which merely gives rise to a shift of the Stoner criterion at $T=0$. It can be simply considered as a renormalization of the Stoner parameter I. Strictly speaking, λ_0 does depend on temperature via χ_0, but its temperature dependence can be neglected compared to that of λ_1. Namely, one can show that $\lambda_1 \propto T^{4/3}$ compared to the T^2 dependence of χ_0 [10]. Important is that due to this temperature dependence of λ_1 the Curie temperature is effectively lowered compared to Stoner theory:

$$T_C \propto E_F\left[I\rho(E_F)-1\right]^{3/4} \approx \left(T_C^S\right)^{3/2}/E_F^{1/2}. \tag{16}$$

In other words, the dynamics of the spin density fluctuations is crucial for the correct description of the Curie temperature.

III. SIZE DEPENDENT ENERGY LEVEL DISTRIBUTION

The SCR theory described above will be used further to calculate the Curie temperature of metallic clusters as a function of their size. Note that the transverse dynamic magnetic susceptibility of a non-interacting system is in fact the only input required for this calculation. For clusters this quantity substantially differs compared to the bulk due to the differing energy level spectrum. The exact calculation of the energy spectrum of a cluster with a given size is actually impossible due to certain randomness of its shape. To overcome this problem, the random matrix theory [16–20] is typically used.

In principle it is possible to calculate the well defined energy levels of an individual small particle. For the case of a perfect metallic sphere this is actually quite obvious. One obtains an energy level spectrum consisting of highly degenerate energy levels, where the separation between the *groups* of the energy levels is proportional to $\frac{1}{L^2}$ with L the diameter of the sphere and the high degeneracy is due to the high geometric symmetry. It is worthwhile to stress, however, that although the nonzero level splitting is proportional to $\frac{1}{L^2}$, the *average* energy level separation around the Fermi level follows the well known $\frac{1}{V} \propto \frac{1}{L^3}$ proportionality (with V the volume).

Obviously the situation of the perfect sphere is very special. However, there are examples of clusters with high geometric symmetry [9]. These are quasi-spherical clusters with so called "magic" numbers $\bar{N} = \bar{N}_m$, where $\bar{N}$ is the number of atoms. For example $\bar{N}_m = 13$, 55 and 147 for the Mackay icosahedron, where each "magic" number corresponds to the right number of atoms so that a spherically shaped cluster can be formed by packing the Mackay icosahedrons in the proper way. Characteristic for the energy level spectrum of these "magic" clusters is the shell structure. These are highly degenerate or close groups of energy levels, which causes the energy level separation near the Fermi level to be rather small. The effects of this shell structure on the electronic pairing in superconductors has been discussed in Ref. 9. For the Curie temperature of the magic clusters the smaller energy level separation around the Fermi level could have important consequences, too.

Here a generic case will be considered only, meaning that the situation of the highly geometrically sym-

metric clusters is excluded. It is assumed that there are uncontrollable atomic surface irregularities, which are sufficient to split apart this large degeneracy of the energy levels. Further, it is assumed that the clusters are large enough to satisfy the proportionality $\delta = 1/\rho(E_F) \propto 1/V$, where δ is the average energy level spacing around the Fermi level and V is the volume of the cluster [17–19]. Thus, considering an ensemble of clusters of the same size, they will differ in their energy level spectrum due to the uncontrollable surface, but have the same average energy level spacing around the Fermi level.

Gor'kov and Eliashberg [21] were the first who recognized that this situation is similar to the interpretation of nuclear energy level spectra discussed by Wigner and Dyson [20]. The idea was to circumvent the unknown and complex interactions between the nucleons by using a statistical description leading to an energy level distribution. To be more specific, it was assumed that the eigenvalues of a random matrix could be taken as a model for the energy levels of a complex nuclear system. This means that an ensemble of possible nuclear systems corresponds to an ensemble of random matrices. Important to remark is that the randomness of each matrix is restricted, because they must possess certain transformation properties imposed by the symmetries that each individual Hamiltonian is supposed to have in common. Then, depending on the imposed symmetry properties different energy level distributions can be derived [20].

In the same manner as described above the uncontrollable surface irregularities can be interpreted as giving rise to a random matrix treatment. For metallic clusters the transformation properties of the random matrix are determined by the magnitude of the spin-orbit coupling H_{so} and the magnitude of the Zeeman splitting in an external magnetic field $2\mu_B\tilde{H}$ compared to δ. For example for small H_{so} and small $2\mu_B\tilde{H}$ compared to δ the matrix must have respectively rotational and time-reversal invariance [16–20]. This example corresponds to the so called Orthogonal ensemble, which is used in this work. The other possible ensembles are given in Table I.

TABLE I: overview of different Hamiltonian symmetries relevant for energy level distribution

Probability distribution	**Magnetic field**	**Spin-orbit coupling**
Poisson	Large	Small
Orthogonal	Small	Small
	Small	Large (even particles)
Unitary	Large	Large
Sympletic	Small	Large (odd particles)

The Poisson ensemble is typical for systems with a regular classical motion, there is no level repulsion in this case. In the case of chaotic system (three other ensembles in Table I) the probability to find two levels with close energies is suppressed. By taking a proper average over the ensemble of the random Hamiltonian matrices, one can obtain an energy level distribution satisfactorily for the cluster system [16, 19, 20]. The result is

$$P_N(E_1,\ldots,E_N) = C_N^{\gamma}\exp\left(-\frac{\kappa}{2\delta^2}\sum_j E_j^2\right)\prod_{j<k}|E_j - E_k|^{\gamma}, \tag{17}$$

where P_N is the probability to find a certain energy level spectrum, $\gamma = 1, 3$ and 4 correspond, respectively, to orthogonal, unitary and sympletic ensemble, C_N^{γ} follows from the normalization condition and κ is an ensemble dependent constant [16]. From the product in equation (17) the level repulsion can be clearly seen.

A very important quantity is $R(|E|)$, which can be derived from the energy level distribution (17) and gives the probability to find two energy levels separated by an energy E independent of the number of energy levels in between them [16]. For the orthogonal ensemble this distribution is given by

$$\begin{aligned} R(|E|) =& 1 - \left(\frac{\sin\left(\frac{\pi E}{\delta}\right)}{\frac{\pi E}{\delta}}\right)^2 \\ &- \frac{d}{d\left(\frac{E}{\delta}\right)}\left(\frac{\sin\left(\frac{\pi E}{\delta}\right)}{\frac{\pi E}{\delta}}\right)\int_{\frac{E}{\delta}}^{\infty}\frac{\sin(\pi x)}{\pi x}dx. \end{aligned} \tag{18}$$

This expression will be used in the following Section for the calculation of the transverse dynamic magnetic susceptibility for a cluster.

Until this point no comments were made about the correctness of the random matrix theory or the assumption that the energy level distribution in an irregular cluster is universal and depends only on the symmetry class. At this point one can say that it is still a hypotheses that needs to be tested more in order to reach complete understanding of the situation. However, at the moment there are many experiments that appear to confirm this theory. [17–19]

IV. RESULTS AND DISCUSSIONS

In this paragraph the Curie temperature of clusters as function of their size is calculated. From Eq. (14) it is clear that this size dependence could come from χ_0 and λ. First the size effect on χ_0 will be considered, second that on λ and finally the resulting effect on the Curie temperature.

With the use of the probability distribution (17) it is possible to calculate the static magnetic susceptibility for a cluster system. In Ref. 21 an interpolation scheme between the regimes $T \ll \delta$ and $T \gg \delta$ (or bulk) has been suggested for which both well developed approximations exist [18, 22]. The important result of these calculations [17, 18, 22], which will be used later on, is that already for $T > \delta$ (we do not mean strong inequality here!) the static magnetic susceptibility of a cluster can be approximated by that of the bulk.

Before λ can be calculated, an expression for the transverse dynamic magnetic susceptibility of a cluster system has to be found. We will follow analysis originally proposed in Ref. 21 for the case of optical polarizability (further this result has been slightly corrected, see for review Ref. 17). The starting point is the general expression for the transverse dynamic magnetic susceptibility,

$$\chi_0^{-+}(\omega,q)=\sum_\mu\sum_\nu\frac{n(E_\nu)-n(E_\mu)}{E_\mu-E_\nu-\omega+i0}\left|\left\langle\nu\left|e^{i\vec{q}\cdot\vec{r}}\right|\mu\right\rangle\right|^2, \tag{19}$$

where $|\nu\rangle$ and $|\mu\rangle$ are eigenstates of the system and $n(E)$ is the Fermi function. Equation (19) accounts for a single particle. Therefore, for the Orthogonal ensemble under consideration, one has to average over the energy level distribution given in equation (17) (with $\gamma=1$). One can then derive that this comes down to multiplying each term in the sum of equation (19) by $\frac{R(|E_\nu-E_\mu|)}{\delta^2}dE_\nu dE_\mu$. For later convenience the expression for the transverse dynamic magnetic susceptibility of an Orthogonal ensemble of clusters $\tilde{\chi}_0^{-+}(\omega,q)$ can be written as

$$\tilde{\chi}_0^{-+}(\omega,q)=\iint dEdE'\iint dE_\mu dE_\nu\delta(E-E_\mu)\delta(E'-E_\nu)\times\left|\left\langle\nu\left|e^{i\vec{q}\cdot\vec{r}}\right|\mu\right\rangle\right|^2\frac{n(E')-n(E)}{E-E'-\omega+i0}\frac{R(|E'-E|)}{\delta^2}. \tag{20}$$

For $\omega\ll E_F$, which will occur naturally for the calculation of λ at the Curie temperature (Section II), it was shown in Ref. 21 that the matrix element is approximately energy independent leading to a separation of the q and ω dependencies:

$$\tilde{\chi}_0^{-+}(\omega,q)=A_{\vec{q}}\iint dEdE'\frac{n(E')-n(E)}{E-E'-\omega+i0}\frac{R(|E'-E|)}{\delta^2},$$
$$A_{\vec{q}}=\iint dE_\mu dE_\nu\delta(E_F-E_\mu)\delta(E_F-E_\nu)\left|\left\langle\nu\left|e^{i\vec{q}\cdot\vec{r}}\right|\mu\right\rangle\right|^2. \tag{21}$$

An accurate computation of this q-dependence or matrix element is difficult. However, for $q_c\ll q\ll k_F$ ($q_c\propto 1/R$ is the inverse average radius of the cluster) the q-dependence can be approximated by that of the bulk, because classical trajectories of electrons in this case are mainly like in the bulk, with rare reflections at the border. Thus, within this q-regime the real and imaginary part of the dynamic susceptibility are in highest order proportional to, respectively q^2 and $1/q$ (Eq. (13)). [10]

For the ω-dependent part of equation (21) it can be shown that it equals the complex function

$$A(\omega)=2\frac{\omega^2}{\delta}\int\frac{R(|E|)}{E^2-(\omega+i0)^2}dE. \tag{22}$$

Besides the approximation of the matrix element, the restriction of the q regime ($q_c\ll q\ll k_F$) has two other important consequences, one for the evaluation of Eq. (12) and the other for Eq. (22). Here the former will be discussed first, because the latter will follow from it.

In this regime ($q_c\ll q\ll k_F$) the sum over q in Eq. (12) can be replaced by an integral, because the integrand is a smooth function with a maximum at approximately $q\propto\omega^{1/3}$, and relevant frequencies are of order of temperature (here we use units $\hbar=k_B=1$). For the remaining part of the sum it is assumed that no singularities occur. Therefore, it is proportional to $1/R$ and can be neglected for large enough cluster sizes.

We will thus restrict ourselves only to the case of not too small clusters, where $\omega\gg\delta$ for relevant ω, otherwise, the discreteness of q-vectors for spin fluctuations is essential, replacement of sum over q by integral is impossible, and the problem should be solved numerically for a given particular shape of the cluster. In this limit one can show that the ω-dependence of the real part of Eq. (22) can be neglected compared to that of the imaginary part. Then, the following expression for the transverse dynamic magnetic susceptibility (normalized to the static susceptibility) of a cluster system can be obtained

$$f_0(\omega,q)=1-Aq^2+iC\frac{\omega}{q}\frac{A_2(z)}{z}. \tag{23}$$

Here A and C are the same constants as for the bulk (equation (13)), $z=2\pi\omega/\delta$, the zero in the subscript of the function f corresponds to $M=0$ (Curie temperature is found from divergence of susceptibility in paramagnetic regime) and A_2 is the imaginary part of the function $A(\omega)$ (22) given by

$$A_2(z)=2\eta-\frac{2\sin^2(\eta)}{\eta}+2\eta\left[\int_0^\eta\frac{\sin(t)}{t}dt-\frac{\pi}{2}\right]\frac{d}{d\eta}\left(\frac{\sin(\eta)}{\eta}\right), \tag{24}$$

where $\eta=z/2$. At $z\to\infty$ $A_2(z)/z\to 1$ giving extrapolation to the bulk (Figure 1).

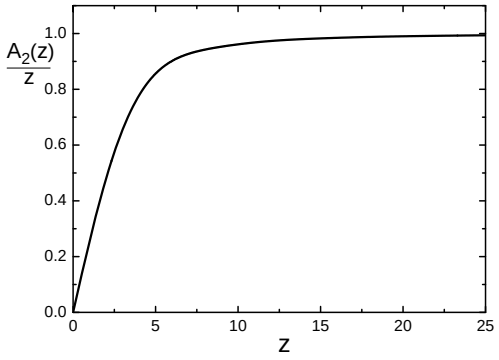

FIG. 1: The function A_2/z as a function of z.

At this point it is possible to estimate the cluster sizes for which the above described approximations are valid.

For this purpose our condition $\omega \gg \delta$ and $\omega \propto T$ can be used, where the last proportionality can be easily derived from the calculation of the temperature dependence of λ_1 (equation (15)). Then, using an estimation $\delta \approx E_F/N$ with N the total number of electrons for the situation where $E_F = 10^4$K and, say, the value $T_c = 20$K typical for weak itinerant ferromagnets [10] results in $N > 500$. Thus, for five d-electrons per atom this would lead to the condition that the above described considerations are valid for clusters containing approximately more than 100 atoms.

As was mentioned, in the case $T \gg \delta$ the static magnetic susceptibility can be approximated by that of the bulk (Eq. (6)) [22]. This means that the important size dependent contribution to the Curie temperature must come from the λ_1 term only. It can be derived by substitution of Eqs. (6) and (23) into Eq. (12) and by approximating the numerators of Eq. (12) by their static long wave-length limit, λ_1 (here called $\lambda_{cluster}$), that is,

$$\lambda_{cluster} \propto T^{4/3} \int_0^\infty dx \frac{x^{1/3}}{e^x - 1} \left(1 - \left[\frac{\sin\left(\frac{\pi x T}{\delta}\right)}{\frac{\pi x T}{\delta}} \right] + \left[\int_0^{\frac{\pi x T}{\delta}} \frac{\sin(t)}{t} dt - \frac{\pi}{2} \right] \left(\frac{\cos\left(\frac{\pi x T}{\delta}\right)}{\frac{\pi x T}{\delta}} - \frac{\sin\left(\frac{\pi x T}{\delta}\right)}{\left(\frac{\pi x T}{\delta}\right)^2} \right) \right)^{1/3} . \quad (25)$$

It is justified since for the case of weak itinerant ferromagnets the region of small q and ω is dominant in the integral (12).

The result for $\lambda_{cluster}$ is presented as a function of T/δ in Figure 2.

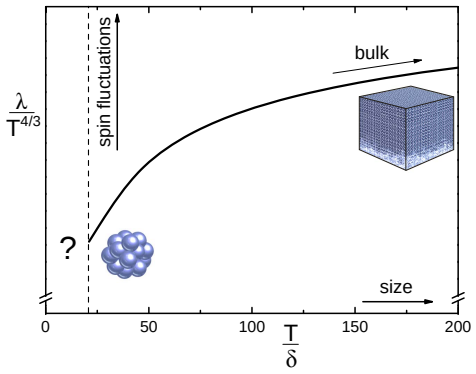

FIG. 2: (color online) The function $\lambda_{cluster}/T^{4/3}$ as a function of T/δ, indicating the increase of the influence of spin fluctuations at higher temperatures and particulary larger sizes. The question mark indicates the applicability limit of our assumptions.

Obviously, for $\delta \to 0$ the constant bulk value ($\frac{\lambda_{bulk}}{T^{4/3}} = B$) is reached. Further, it is important to notice that a cluster system for a fixed size (or δ) has a larger temperature dependence compared to the bulk which leads to an increase of the Curie temperature. For smaller clusters the enhancement of the Curie temperature will be larger.

It is instructive to show the data in a slightly different way, where λ is plotted as an function of temperature for different sizes ($\delta = 0$, 0.1 and 1.0 in units of K) as can be seen in Figure 3. To summarize, the results for the Curie temperature of the cluster normalized to the

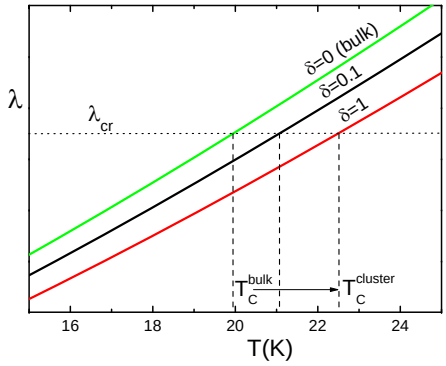

FIG. 3: (color online) The function λ_{bulk} (or $\delta = 0$) and $\lambda_{cluster}$ for $\delta = 0.1$ and 1 is plotted as function of temperature. Here δ is given in units of K and λ_{cr} is the critical value of λ, where the net magnetization becomes zero.

Curie temperature of the bulk is plotted in Figure 4 as a function of the average energy level spacing normalized to the Curie temperature of the bulk. The increase of the Curie temperature for smaller cluster sizes is caused by the increasing suppression of spin density fluctuations for smaller sizes. In Section II it was shown that the function λ takes into account the influence of the spin fluctuations on the Curie temperature.

To verify this theory quantitatively experiments on weakly itinerant clusters should be performed. We believe, however, that qualitatively our conclusion is correct even beyond the limit of formal applicability of the SCR theory (equation (8)). The level repulsion *should* suppress spectral density of spin fluctuations at small frequencies, and this *should* be the main effect in the temperature dependence of magnetic properties, these statements being quite general. The experiments on Fe, Co and Ni mentioned in the Introduction [4–6] seem to

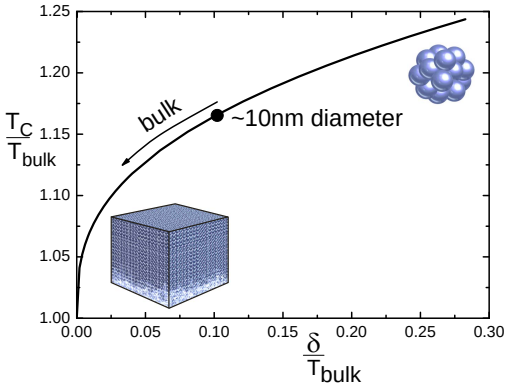

FIG. 4: (color online) Curie temperature of a cluster system normalized to the Curie temperature of the bulk as a function of the average energy level spacing also normalized to the bulk Curie temperature.

be in agreement with our conclusion.

It would be interesting to improve this theory further for smaller cluster sizes. For this purpose the discreteness of the energy spectrum should be explicitly taken into account and the influence of the static susceptibility will become important. For clusters even smaller so that $\delta \propto 1/V$ is not applicable anymore random matrix theory will fail. In this regime probably ab initio approaches are the only way out.

To conclude, small particles of itinerant magnets show an increase of their Curie temperature when reducing their size, in a clear contrast to what one would expect for a localized picture. Such enhancement of magnetic stability originates from the size induced renormalization of electronic states leading to a suppression of spin fluctuations, and may open interesting perspectives for application of such systems in nanotechnology.

Acknowledgments

Funding from the European Community's Seventh Framework Programme (FP7/2007-2013 Grants No. NMP3-SL-2008-214469 (UltraMagnetron) and No. 214810 (FANTOMAS)] is gratefully acknowledged. M. I. K. acknowledges a financial support by the EU-India FP-7 collaboration under MONAMI.

[1] S. N. Khanna and A. W. Castleman, *Quantum Phenomena in Clusters and Nanostructures* (Springer, Berlin, 2003)
[2] M. Karkare, *Nanotechnology Fundamentals and Applications* (I. K. International Publishing House Pvt. Ltd., New Delhi, 2008)
[3] S. Sugano and H. Koizumi, *Microcluster Physics* (Springer, Berlin, 1998)
[4] F. Liu, S. N. Khanna, and P. Jena, Phys. Rev. B**43**,8179 (1990)
[5] J. P. Bucher, D. C. Douglass, and L. A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1991)
[6] I. M. L. Billas, J. A. Becker, A. Chatelain, and W. A. de Heer, Phys. Rev. Lett. **71**, 4067 (1993)
[7] A. J. Cox, J. G. Louderback, and L. A. Bloomfield, Phys. Rev. Lett. **71**, 923 (1993)
[8] M. B. Nickelbein, Phys. Rev. Lett. **86**,5255 (2001)
[9] V. Z. Kresin and Y. N. Ovchinnikov, Phys. Rev. B **74**, 024514 (2006)
[10] T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer, Berlin, 1985)
[11] F. Aguilera-Granja and J. L. Morá n-L ó pez, Solid State Comm. **74**, 155 (1990)
[12] V. Yu. Irkhin, A. A. Katanin and M. I. Katsnelson, J. Magn. Magn. Mater. **164**, 66 (1996)
[13] A. I. Lichtenstein, M. I. Katsnelson, and G. Kotliar, Phys. Rev. Lett. **87**, 067205 (2001)
[14] M. I. Katsnelson, V. Yu. Irkhin, L. Chioncel, A. I. Lichtenstein, and R. A. de Groot, Rev. Mod. Phys. **80**, 315 (2008)
[15] I. E. Dzyaloshinskii and P. S. Kondratenko, Sov. Phys.-JETP **43**, 1036 (1976)
[16] F. J. Dyson, J. Math. Phys. **3**, 140 (1962)
[17] J. A. A. J. Peerenboom, P. Wyder, and F. Meijer, Phys. Rev. **78**, 173 (1981)
[18] W. Halperin, Rev. Mod. Phys. **58**, 533 (1986)
[19] H. J. Stöckmann, *Quantum Chaos: An Introduction* (Cambridge University Press, Cambridge, 2000)
[20] A. Bohr and B. Mottelson, *Nuclear Structure, Vol 1: Single-Particle Motion* (W. A. Benjamin, New York, 1969)
[21] L. P. Gor'kov and G. M. Eliashberg, Sov. Phys.-JETP **48**, 1407 (1965)
[22] R. Denton, B. Mühlschlegel, and D. J. Scalapino, Phys. Rev. B **7**, 3589 (1973)