Fizika Nizkikh Temperatur, 2001, v. 27, Nos. 9/10, p. 1214–1220

Ortnogonal-to-unitary ensemble crossover in the electronic specific heat of metal namoclusters

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Received August 27, 2001

We present a theoretical and experimental study on the influence of a magnetic field on the energy-level statistics in metal nanoparticles. Based on the random-matrix theory, a gradual field-induced crossover behavior is predicted from the orthogonal to the unitary ensemble. Experimental data of the electronic specific heat of metal nanoparticles for different fields in the quantum-size temperature regime compare favourably with these theoretical (analytical) predictions.

PACS: **65.40.+g**, **71.24.+q**, 73.61.Tm

1. Introduction

A large number of papers have been devoted to the experimental and theoretical investigation of the thermodynamic properties of small metal particles (nanoclusters), in order to test the predictions based on the random-matrix theory of the energy-level statistics (for reviews see [1–4]). The discrete character of the energy spectrum of a nanocluster can be regarded as a direct manifestation of the quantum size effect. The Wigner–Dyson [5,6] random ensemble description relies upon the functional $\mathcal{P}(\mathcal{H})$:

$$\mathcal{P}(\mathcal{H}) \propto \exp\,[-\nu\ \mathrm{Tr}V(\mathcal{H})]\ . \qquad (1)$$

This functional is chosen to describe the probability distribution for the random ensemble of $N \times N$ Hamiltonian matrices of the electrons in the nanoclusters. An ensemble is called Gaussian if $V(\mathcal{H}) \propto \mathcal{H}^2$. This distribution is successfully used in the absence of strong electron-electron correlations [1,2]. In the Gaussian distribution the argument of the exponential becomes a simple sum over all the matrix elements: $\mathrm{Tr}\ \mathcal{H}^2 = \sum\limits_{ij} |\mathcal{H}_{ij}^2| = \sum\limits_i E_i^2$, so that it does not contribute to the correlations between the levels $\{E_i\}$, because the probabilities for the different E_i's factorize:

$$\mathcal{P}(\mathcal{H}) \propto \exp[-\nu \mathrm{Tr}\ \mathcal{H}^2] \propto \prod_i \exp[-\nu E_i^2] = P(\{E_n\})\ . \qquad (2)$$

Therefore, the spectral correlations in the Gaussian ensemble are purely geometrical in their nature [1], since they follow solely from the Jacobian $J(\{E_n\})$ [3]:

$$J(\{E_n\}) = \prod_{i<j} |E_i - E_j|^{\nu}\ . \qquad (3)$$

The term «geometrical» used above is based on the fact that the Jacobian relates volumes in the two equivalent abstract spaces of the random variables, thus reflecting their geometrical structure:

$$\mathcal{P}(\mathcal{H}) d\mu(\mathcal{H}) = d\mu(U) \left(P(\{E_n\}) J(\{E_n\}) \prod_i dE_i \right). \qquad (4)$$

Here the volume element $d\mu(\mathcal{H})$ is the «natural» volume measured in the space of the Hermitian

matrix elements $\mathcal{H}_{ij}$, which factorizes into the product $d\mu(U)\prod_i dE_i$ of the volume elements $d\mu(U)$ and $\prod_i dE_i$ in the subspaces of the eigenvectors and eigenvalues of the matrix $\mathcal{H}$. As is apparent from Eq. (3) and (4), the character of the statistical distribution of the level-spacings depends only on the index ν [7], which counts the number of degrees of freedom in the matrix elements $\mathcal{H}_{ij}$. This number reflects the symmetry of the system in question and can only take the values 1, 2 or 4 for the real, complex or real quaternion matrix elements, respectively. The matrix elements may be chosen real when time-reversal symmetry exists, while they become imaginary when this symmetry is broken, e.g., by an external magnetic field or magnetic impurities. In time-reversal symmetric systems with broken spin-rotation symmetry, e.g., as a consequence of spin-orbit interaction, the matrix elements are real quaternions. The details of the interactions inside the system do not change these general symmetries, and hence, the spectral correlations possess universality. The corresponding Gaussian ensembles of random matrices, depending on their symmetry, are called orthogonal ($\nu = 1$), unitary ($\nu = 2$) or symplectic ($\nu = 4$) ensembles respectively, or in the abbreviated form: GOE, GUE or GSE. Thus, the symmetry of the Hamiltonian matrices of the clusters changes either from GOE to GUE, or from GSE to GUE upon application of an external magnetic field. We remark that the consequences of random perturbations on the energy level spectra of an assembly of small metal particles and the ensuing thermodynamic properties were first investigated by Kubo [8], using the Poisson distribution for the energy level statistics. Shortly afterwards, Gor'kov and Eliashberg [9] pointed out the relevance of the Wigner–Dyson formalism for small metal particles and demonstrated the profound influence of the level repulsion on the low-temperature thermodynamics of the small metal particles in the two limiting cases of GOE and GUE. A more detailed consideration of the metal-cluster thermodynamics in these two limits was later made in [10]. Theoretical justification of the Wigner–Dyson statistics was provided in [11] for the case of diffusive (nonballistic chaotic) electron motion inside the cluster. The most recent theoretical achievements, which include justification of the Wigner–Dyson statistics for the nonintegrable chaotic systems, «ballistic billiards», with random scattering at the boundaries, are summarized in [1].

In this note we present a preliminary report on detailed theoretical predictions [12], together with a comparison to recently obtained experimental data [13–15], for the specific heat behavior of metal nanoclusters in the crossover regime induced by an external magnetic field. The crossover manifests itself as a gradual transition from the orthogonal to unitary Gaussian distribution of the electronic energy levels (GOE-to-GUE transition) of the nanoclusters. We remark that these measurements represent the first experimental observation of the presence of the quantum-size effect in the electronic specific heat and susceptibility of metal nanoparticles.

Mathematically, the basic change resulting from the GOE-to-GUE crossover lies in the appearance of the (random) imaginary part of the electron Hamiltonian matrix due to the breaking of the time-reversal symmetry by the external magnetic field. This phenomenon was modeled by Pandey and Mehta [16] by the addition of a random antisymmetric real matrix $\mathcal{A}$ with imaginary weight $i\alpha$ to the real symmetric Hamiltonian matrix $\mathcal{H}_0$:

$$\mathcal{H} = \mathcal{H}_0 + i\alpha\mathcal{A}. \tag{5}$$

The parameter α is proportional to the magnetic flux Φ through the system, i.e., through the nanoparticle, so that the relation between α and Φ depends on the geometry of the particle and on the ratio of its size (radius R) to the electron mean free path l. For a ballistic sphere ($R << l$) with diffuse boundary scattering of electrons this relation is [2]:

$$N\alpha^2 = \left(\frac{e\Phi}{h}\right)^2 \frac{\hbar v_F}{R\delta}\,\frac{8\pi}{45}, \tag{6}$$

where v_F is the Fermi velocity, δ is the mean level spacing at the Fermi energy of the nanoparticle, and N is the matrix dimension indicating the total number of the single-electron states taken into account in the model of the nanoparticle. The addition of an independently randomly distributed matrix $\mathcal{A}$ to the (random) real symmetric matrix $\mathcal{H}_0$, effectively doubles the number of degrees of freedom in the elements of the Hamiltonian matrix $\mathcal{H}$, so that the Gaussian distribution of $\mathcal{H}$ takes the form:

$$\mathcal{P}(\mathcal{H}) \propto \exp\left(-\sum_{i,j}\left[\frac{\mathcal{H}_{0ij}^2}{4v^2} + \frac{\mathcal{A}_{ij}^2}{4v^2}\right]\right). \tag{7}$$

Here the variance v^2 determines the mean level spacing $\delta = \pi v/\sqrt{N}$ in the vicinity of the Fermi energy of the cluster in the limit $N >> 1$ and $\alpha << 1$. As was explained above, the doubling of the dimensionality of the phase-space of the off-dia-

gonal matrix elements leads [16] in turn to the doubling of the exponent ν in the eigenvalue (level) distribution function $P(\{E_n\})$, from $\nu = 1$ in GOE to $\nu = 2$ in GUE:

$$P_{GOE}(\{E_n\})J_{GOE}(\{E_n\}) \propto \prod_{i<j} |E_i - E_j| \prod_k \exp[E_k^2] \rightarrow$$

$$\rightarrow \prod_{i<j} |E_i - E_j|^2 \prod_k \exp[-2E_k^2] \propto P_{GUE}(\{E_n\})J_{GUE}(\{E_n\}) \,. \tag{8}$$

The subtle feature of this crossover is that the doubling of ν is actually energy-dependent [2]. The GOE-to-GUE transition is completed on the energy scale E if $|\delta E_i| \geq E$, where δE_i is the energy shift due to the «perturbation» $i\alpha\mathcal{A}$ in the Hamiltonian (5):

$$\delta E_i = \alpha^2 \sum_{i \neq j} \frac{\mathcal{A}_{ij}^2}{E_i - E_j} \,. \tag{9}$$

Simultaneously, the «high-energy» part of the spectrum on the scale $E >> \delta E_i$ remains distributed according to the upper line of Eq. (8) with $\nu = 1$, as it would be in the case of an orthogonal ensemble. Therefore, measuring the thermodynamic properties of the nanoparticles in the external magnetic field may give an experimental verification of the relation (8) and of the gradual nature of the GOE-to-GUE transition, provided that these properties depend on the different energy scales at the different temperatures.

On basis of the above discussion we expect the specific heat of the nanoclusters to be a relevant thermodynamic characteristic for the observation of the GOE-to-GUE crossover in magnetic field. In order to investigate this problem quantitatively, we consider an ensemble of metal particles with half of the clusters having an even number of electrons and the other half having an odd number. Our calculation was done [12] in the low temperature limit, $T << \delta$, so that only a few electronic levels need to be explicitly considered. Taking into account all the different possibilities of the formation of the lowest excited energy states, one finds the following expressions for the low-temperature partition functions of the even and odd clusters, Z_{even} and Z_{odd} respectively:

$$Z_{\text{even}} = (1 + 2e^{-\beta\delta} \cosh(h\beta))(1 + 2e^{-\beta\delta}) + O(e^{-2\beta\delta}), \tag{10}$$

$$Z_{\text{odd}} = 2 \cosh(h\beta/2)(1 + 2e^{-\beta\delta}) + O(e^{-2\beta\delta}) \,, \tag{11}$$

where $\beta = 1/T$ is the inverse temperature in energy units, i.e. taking $k_B = 1$. Also $h = g\mu_B H$, where μ_B is the Bohr magneton, $g = 2$ is the Landé factor, and H is the external magnetic field.

Using Eqs. (10) and (11) we have for the free energy F

$$F = -\frac{1}{2} T(\ln Z_{\text{even}} + \ln Z_{\text{odd}}) \,, \tag{12}$$

where the coefficient $1/2$ represents the fifty/fifty probability to find an even/odd cluster in the macroscopically large assembly of otherwise identical metal particles.

The specific heat C_V, magnetization M, and magnetic susceptibility χ can be derived from the well-known relations

$$C_V = -T \frac{\partial^2 F}{\partial T^2} \,, \quad M = -\frac{\partial F}{\partial H} \,, \quad \chi = -\frac{\partial^2 F}{\partial H^2} \,. \tag{13}$$

In the simplest equidistant model for a metal nanoparticle, due to Fröhlich [17], in which all the levels are at a constant interlevel spacing δ, these thermodynamic functions are given by the formulae:

$$C_V = \frac{1}{8}(h\beta)^2 \frac{1}{\cosh^2(h\beta/2)} + 2(\delta\beta)^2 \frac{e^{-\delta\beta}}{(1 + 2e^{-\delta\beta})^2} +$$

$$+ \frac{1}{2}\beta^2 \frac{4h^2 e^{-2\delta\beta} + (h - \delta)^2 e^{\beta(h-\delta)} + (h + \delta)^2 e^{-\beta(h+\delta)}}{(1 + 2e^{-\delta\beta}\cosh(h\beta))^2} \,, \tag{14}$$

$$M = g\mu_B \left[\frac{1}{4}\tanh(h\beta/2) + \frac{\sinh(h\beta)}{e^{\delta\beta} + 2\cosh(h\beta)}\right], \tag{15}$$

$$\chi = \beta(g\mu_B)^2 \left[\frac{1}{8\cosh^2(h\beta/2)} + \frac{2 + e^{\delta\beta}\cosh(h\beta)}{(e^{\delta\beta} + 2\cosh(h\beta))^2}\right]. \tag{16}$$

It is obvious from the above expressions that in the equidistant model there is effectively a gap in the density of states at the Fermi-level, leading to an exponentially vanishing specific heat at low enough temperatures, i.e. $T << \delta$. The opposite extreme to the current model is the Poisson level distribution $P_0(E_i - E_j) \propto \exp[-|E_i - E_j|/\delta]$, corresponding to no gap at all, which was used by Kubo [8]. Unlike in the distributions (8), the Poisson's distribution entails a finite probability for the two levels to «stick together», thus neglecting the level repul-

sion. Hence, the pseudo-gap in the density of states at the Fermi-energy, caused by the off-diagonal random matrix elements between different electronic states in the cluster, disappears in the Poisson model.

2. Averaging over the level distribution in the crossover region

Our aim here is to obtain more realistic expressions for the thermodynamic functions of the metal nanoclusters than those given in Eqs. (14), (15), and (16), which were derived for an equidistant model of the energy levels. Actually, for small particles one usually assumes that minor perturbations such as surface irregularities (even of an atomic scale) will be sufficient to make the level distribution random. Here we will suppose the random distribution to obey the Wigner–Dyson Gaussian ensemble statistics. Indeed, the published experimental data [14] for the temperature dependences of the specific heat of the metal nanoparticles clearly showed the inapplicability of the equal level spacing model, in which case the specific heat becomes exponentially small at the temperatures $T << \delta$. Comparison of the experimental curves in [14] with the theory leads to the conclusion that the experimental behavior has to be described by a model based on a non-vanishing probability of even the smallest level spacings. When these spacings are much less then the average distance between the levels (δ), they will make essential contributions to the specific heat at the lowest temperatures, $T << \delta$, so that the energy gap due to the quantum size effect becomes a pseudo-gap. Then, the explicit averaging over the appropriate level distribution is essential to describe the data.

It proved to be possible to perform such an averaging analytically [12] for the case of the low enough temperatures, where only the lowest excited states of the clusters should be important. The approximation used here consists in the averaging of the low-temperature thermodynamic functions $A(\delta, T, H)$, found for the equidistant model, with the two-level correlation function R_2. For this purpose we substitute an equidistant level spacing δ by a random variable ϵ and then perform an integration over this variable:

$$\overline{A}(T, H, \delta) = \int_0^\infty R_2\left(\frac{\epsilon}{\delta}\right) A(\epsilon, T, H)\, d\left(\frac{\epsilon}{\delta}\right). \quad (17)$$

Let the level distribution function $p_n(x)$ define the probability to find a spacing x between two energy levels, while there are n other energy levels being located between those two. Here we normalize the random level spacing ϵ by the average interlevel spacing δ near the Fermi-level of a cluster: $x = \epsilon/\delta$. Then, the two-level correlation function is defined as follows:

$$R_2(x) = \sum_0^\infty p_n(x) . \quad (18)$$

At small enough $x << 1$, we have $R_2(x) \to p_0(x)$, and in the limit $x >> 1$, $R_2(x) \to 1$. From the work of Pandey and Mehta [16], using also relation Eq. (6) (see [2]), we have an analytical expression for R_2 for an arbitrary external magnetic field H:

$$R_2(x) = 1 - \left(\frac{\sin(\pi x)}{\pi x}\right)^2 + \frac{1}{\pi^2}\int_0^\pi k \sin(kx)\, e^{2k^2\rho^2}\, dk \int_\pi^\infty \frac{\sin(zx)}{z}\, e^{-2z^2\rho^2}\, dz , \quad (19)$$

where $\rho = 1.15\mu_B H/\delta$ for a spherical particle and where ballistic electron motion inside the particle is supposed [12]. Then, without magnetic field, $\rho = 0$, $R_2(x << 1) \sim x$, while in the strong field limit, $\rho >> 1/\pi$, $R_2(x << 1) \sim x^2$. The probability to find two levels close together, $x << 1$, decreases with the field from $\sim x$ to $\sim x^2$. This effect is called the «interlevel repulsion» in a magnetic field and causes a change of the low-temperature dependence of the field-independent contribution to the electronic specific heat (second term on the right hand side (rhs) of Eq. (14)) from $C_{el}^{GOE} \propto T^2$ for GOE ($H = 0$) to $C_{el}^{GUE} \propto T^3$ for GUE ($\mu_B H >> \delta$) [9,10]. Incidentally, in case of metal nanoparticles with strong spin-orbit coupling (GSE level-statistics), this contribution to specific heat is expected to behave as $C_{el}^{GSE} \propto T^5$ at low enough temperatures [10]. On the other hand, the spin-flip contribution to C_{el} (incorporated in the third term on the rhs of Eq. (14)), after averaging with the function $R_2(x)$, brings T-linear contribution to the electronic specific heat (C_{el}), which masks the crossover in the temperature dependence described above. This later fact, as far as we know, was not considered in the previous works, see [9,10]. Below we present the calculated dependences of C_V on the temperature

and the external magnetic field H and compare them with the recently obtained experimental results.

3. Discussion

As a main result to be concluded from the calculated dependences shown in Fig. 1, we point out that the GOE-to-GUE transition in magnetic field has a gradual crossover character. The underlying reason is that the distribution of the level spacings on the «small energy scale», $\epsilon/h << 1$, obeys GUE statistics already at small fields $h/\delta << 1$, while the level spacings for large energy, $\epsilon/h >> 1$ remain distributed according to GOE until the field becomes strong enough, i.e., $h/\delta \geq 1$. Thus, in small fields, $h/\delta << 1$, the temperature dependence of the specific heat may be separated into three different regions. In the lowest temperature region, $T << h << \delta$, the electronic specific heat $C_{\rm el}$ contains the unitary ensemble part: $C_{\rm el}^{GUE}(T) \propto T^{\alpha}$, with $\alpha = 3$, together with the spin-flip contribution: $C_{\rm el}^{sf}(T) \propto TR_2(h/\delta)$. In the intermediate temperature interval, $h << T << \delta$, the temperature dependence remains the same as in the orthogonal ensemble, i.e., with $\alpha = 2$: $C_{\rm el}(T) \propto T^2$, because the spin-flip contribution in this case merely changes the numerical prefactor in front of T^2. Finally, in the «high temperature» region, $T >> \delta$, the temperature dependence of the electronic specific heat follows the usual Fermi-liquid bulk behavior: $C_{\rm el}(T) \propto T$. Different characteristic regions are clearly seen in Fig. 1, where the contributions to specific heat are plotted separately for the two different magnetic field values as functions of the temperature in units of the average level spacing δ. As can be seen in Fig. 1, in the weakest field, $h = 0.1\delta$, the Schottky contribution due to the odd clusters masks the $C_{\rm el}^{GUE}(T) \propto T^3$ term within a substantial part of the low temperature interval, while the crossover from $\alpha = 3$ via $\alpha = 2$ to $\alpha = 1$ in the higher temperature region is quite pronounced in the upper panel of Fig. 1. In the higher magnetic field $h = 1\delta$ the Schottky peak had moved to higher temperatures, where it is superimposed on the much larger even cluster contribution to the specific heat and so it does not mask substantially the T^3 term in the total $C_{\rm el}$ as in the weakest field case. Nevertheless, the spin-flip contribution, which is $\propto TR_2(h/\delta)$, still masks the T^3 GUE term in the low temperature interval: $T \leq \{h, \delta\}$. In the even stronger magnetic field $h = 1.62\delta$ (not shown in Fig. 1) practically the whole low temperature interval $T << \delta$ is occupied by the unitary ensemble contribution to the specific heat $C_{\rm el}^{GUE}(T) \propto T^3$.

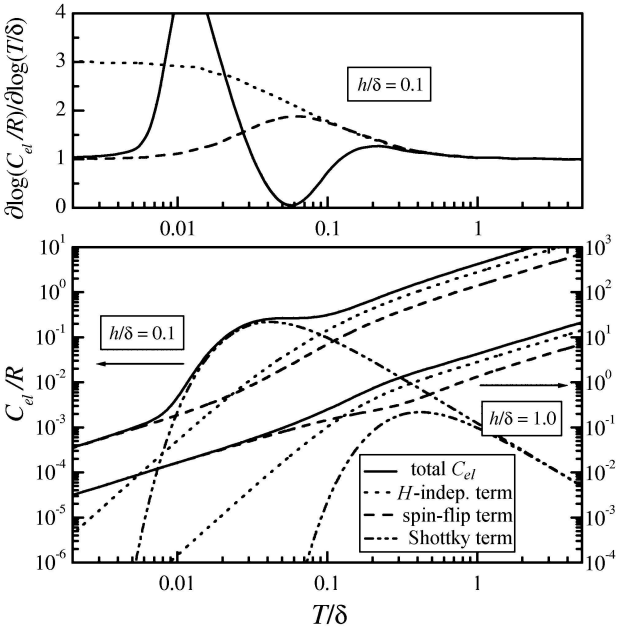

Fig. 1. Calculated temperature dependences of the electronic specific heat $C_{\rm el}$ and its different constituents (lower panel), and of their logarithmic derivatives (upper panel, for $h/\delta = 0.1$ only) for a random Gaussian ensemble of metal clusters at two different values of the external magnetic field H (in units $g\mu_B H/\delta$). The temperature is expressed in units T/δ (putting $k_B = 1$).

The spin-flip term $C_{\rm el}^{sf} \propto T$ is again the strongest one here, as $R_2(h/\delta)$ saturates at $h/\delta >> 1$: $R_2 \to 1$. Hence, the spin-flip term mimics the «bulk» behavior at low temperatures $T \leq \delta < h$. Then, at $T \geq \delta$, $C_{\rm el}(T)$, smoothly crosses-over into the «actual» bulk behavior, $C_{\rm el}(T) \propto T$. The two regions are separated by the Schottky contribution, which in this case could be visible only in the $\partial \ln C_{\rm el}/\partial \ln T$ vs. $\ln T$ dependence, but is hardly noticeable in the $C_{\rm el}(T)$ curve (not shown). Furthermore, based on the above discussion, we would expect a direct crossover from the GOE, $C_{\rm el}(T) \propto T^2$ to the bulk $C_{\rm el}(T) \propto T$ behavior of specific heat in zero magnetic field, where the spin-flip contribution is absent. Indeed, this behavior was measured in a series of Pd metal clusters of different sizes ranging from 2 nm to 15 nm in diameter [13–15], and is shown in Fig. 2. In this figure the electronic contributions to the specific heat are shown, which were obtained at very low temperatures ($T < 1$ K), by subtracting the phonon (lattice) contributions from the measured data. The special feature of these metal clusters is that they appear as part of chemically synthesized, molecular compounds, each compound containing metal clusters of a given uniform size embedded in a stabilizing ligand shell [18–21]. The metal cluster com-

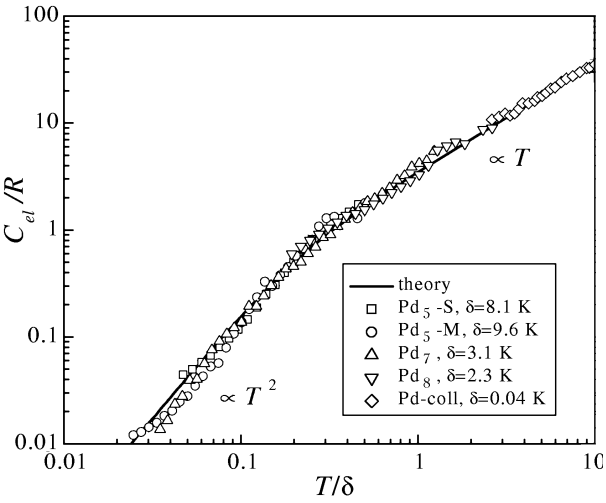

Fig. 2. Electronic specific heat (in zero field) of the metal nanoclusters discussed in the text. Data were scaled on the theoretical prediction (solid curve) with the average energy level spacing δ as the adjustable parameters. The transition from bulk-like behavior ($\propto T$) to quantum-size behavior ($\propto T^2$) can be clearly seen.

pounds mentioned here were made by two different groups, namely that of profs. Moiseev and Vargaftik in Moscow, and the group of prof. G. Schmid at the University of Essen. The compounds indicated by Pd_5 , Pd_7 , and Pd_8 contain respectively 561, 1415, and 2057 Pd atoms per cluster. There are two Pd_5 compounds, namely with chemical formula $Pd_{561}Phen_{60}(OAc)_{180}$ synthesized by Moiseev and Vargaftik (Pd_5-M), and $Pd_{561}Phen_{36}O_{200}$ synthesized by Schmid (Pd_5-S). The chemical formulae of Pd_7 and Pd_8 are $Pd_{1415}Phen^{(bu)}_{114}O_{1650}$ and $Pd_{2057}Cinch_{56}$, respectively. Here, Cinch stands for cinchonidine, Phen for phenanthroline and $Phen^{(bu)}$ is a phenanthroline derivative. The sample denoted by Pd-coll is a Pd colloid with average particle size of $1.25{\cdot}10^5$ atoms/particle and a small size distribution of 5–10%. The Pd_7 and Pd_8 metal clusters compounds and the Pd-coll were also synthesized by Schmid and coworkers.

It is worth pointing out that the only adjustable parameter needed to scale the experimental C_{el} vs. T data upon the theoretical curve in Fig. 2 is the average energy level spacing δ. The values used are given in the figure and indeed vary roughly with the inverse volume of the particles, as expected from theory (the particle diameters are approximately 2.4, 3.2, 3.7, and 15 nm for Pd_5 , Pd_7 , Pd_8 , and Pd-coll, respectively). Accordingly, the crossover from quasi-bulk behavior ($C_{el} \propto T$) to the quantum-size regime ($C_{el} \propto T^2$) near $T/\delta \simeq 0.2$ actually occurs at lower temperature, the larger is the particle. This same trend can also be seen in the experimental field dependence of the specific heat, as shown in Fig. 3. It should be pointed out here that the mere presence of a field dependence is in itself a quantum size effect, since the bulk metal will not show such behavior. Comparing the data of Pd_5 , Pd_7 , and Pd-coll, one observes that the onset temperature of the field-dependence is indeed lower, the larger the particle. We note that the data in Fig. 3 show the raw measurements, i.e., with the lattice contributions not yet subtracted. The latter give a T^3 term, which becomes rapidly negligible below 1 K, as can be seen most clearly from the Pd-coll data. The specific heat behavior of bulk Pd has been included in Fig. 3 as the dotted curves. Comparing this with Pd-coll, one observes that for the latter the linear term is still 20–30% lower than for the bulk, which can be understood in terms of a lower average density of states at the Fermi-energy in the nanoparticles due to surface effects [22].

Finally, Fig. 4 shows the field-dependence measured for Pd_5 on a linear temperature scale, with the phonon contribution subtracted. The zero-field data

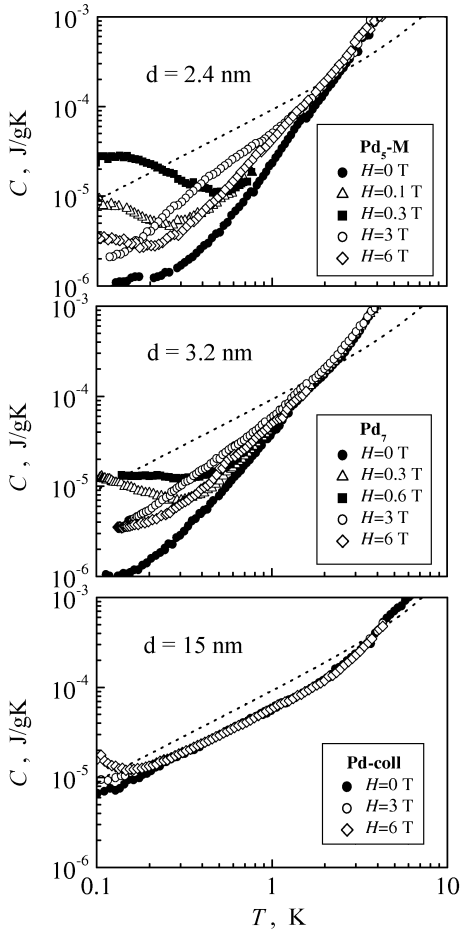

Fig. 3. Temperature dependence of the measured specific heat (including phonon contributions) for Pd_5 , Pd_7 , and Pd-coll. The dotted curves give the behavior found for bulk Pd.

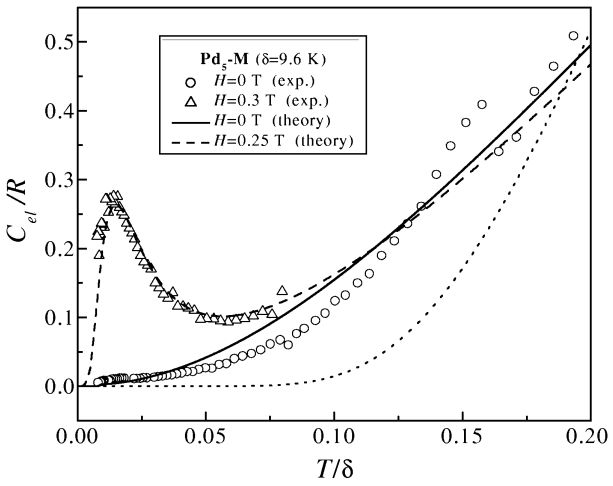

Fig. 4. Temperature dependence of the electronic specific heat of Pd_5 obtained after subtraction of the lattice contribution. Dotted curve: equal level spacing model. The other curves follow from the calculations discussed in the text (compare Fig. 1).

clearly display the T^2 dependence predicted for the GOE model, in contrast with the exponential dependence following from the equal level spacing model (dotted curve). The Schottky anomaly found in low field is ascribed to the odd-electron clusters and is in good agreement with the theoretical prediction (also shown in Fig. 1 for $h/\delta = 0.1$).

In conclusion, we have presented theoretical and experimental results describing the quantum-size effects in the thermodynamic properties of nanosize metal clusters with random distribution of the electronic energy levels in different external magnetic fields in the few-Kelvin temperature range. The experimental data show a good qualitative agreement with theoretical predictions based on the Wigner–Dyson/Mehta–Pandey random-matrix theory.

Acknowledgments

We like to thank prof. G. Schmid for providing the samples quoted in this study. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is sponsored by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

Dedication

It is our great pleasure to dedicate this paper to the memory of prof. Lev Shubnikov, who was a prominent visitor of the Kamerlingh Onnes Laboratory in the last century, where, together with prof. W. J. de Haas, he discovered the famous effect that bears their names. As witnessed by this paper, also recently there have been intensive relations between scientists at the Kamerlingh Onnes Laboratory and the former Sovjet Union. It is our hope that these fruitful collaborations, from which we have had so much profit and pleasure, will be an inspiration for future workers to continue and intensify scientific exchange worldwide.

1. T. Guhr, A. Müller-Groeling, and H. A. Weidenmuller, *Phys. Rep.* **299**, 189 (1998).
2. C. W. J. Beenakker, *Rev. Mod. Phys.* **69**, 731 (1997).
3. W. P. Halperin, *Rev. Mod. Phys.* **58**, 533 (1986).
4. J. A. A. J. Perenboom, P. Wyder, and F. Meier, *Phys. Rep.* **78**, 175 (1981).
5. E. P. Wigner, *Proc. Cambridge Philos. Soc.* **47**, 790 (1951); E. P. Wigner, in: *Statistical Theories of Spectra: Fluctuations*, C. E. Porter (ed.), Academic Press, New York (1965).
6. F. J. Dyson, *J. Math. Phys.* **3**, 1199 (1962); F. J. Dyson and M. L. Mehta, *J. Math. Phys.* **4**, 701 (1963).
7. see C. E. Porter (ed.), *Statistical Theories of Spectra: Fluctuations*, Academic Press, New York (1965).
8. R. Kubo, *J. Phys. Soc. Jpn.* **17**, 975 (1962).
9. L. P. Gor'kov and G. M. Eliashberg, *Sov. Phys. JETP*, **21**, 940 (1965).
10. R. Denton, B. Mühlschlegel, and D. J. Scalapino, *Phys. Rev.* **B7**, 3589 (1973).
11. K. B. Efetov, *Adv. Phys.* **32**, 53 (1983).
12. S. I. Mukhin and O. V. Kurapova, manuscript in preparation.
13. Y. E. Volokitin, *Ph.D. Thesis Leiden University* (March 1997).
14. Y. E. Volokitin, J. Sinzig, L. J. de Jongh, G. Schmid, M. N. Vargaftik, and I. I. Moiseev, *Nature* **384**, 621 (1996).
15. F. L. Mettes, *Ph.D. Thesis Leiden University*, in preparation.
16. A. Pandey and M. L. Mehta, *Commun. Math. Phys.* **87**, 449 (1983).
17. H. Frölich, *Physica* **4**, 406 (1937).
18. M. N. Vargaftik, V. P. Zagorodnikov, I. P. Stolyarov, I. I. Moiseev, V. A. Likholobov, D. I. Kochubey, A. L. Chuvilin, V. I. Zaikovsky, K. I. Zamaraev, and G. I. Timofeeva, *J. Chem. Soc., Chem. Commun.* **937** (1985).
19. G. Schmid, *Chem. Rev.* **92**, 1709 (1992); G. Schmid, *Struct. Bond.* **62**, 5285 (1985).
20. *Clusters and Colloids: From Theory to Applications*, G. Schmid (ed.), VCH, Weinheim (1994).
21. *Physics and Chemistry of Metal Cluster Compounds*, L. J. de Jongh (ed.), Kluwer Academic, Dordrecht (1994).
22. D. A. van Leeuwen, J. M. van Ruitenbeek, and L. J. de Jongh, *Phys. Lett.* **A170**, 325 (1992).