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Influence of chemical disorder on the electronic level spacing distribution of the Ag_{5083} nanoparticle: A tight-binding study

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ABSTRACT

In the present work we study, employing a tight-binding Hamiltonian, the influence of chemical disorder on the electronic level spacing distribution of a silver nanoparticle containing 5083 atoms ($\sim$ 5.5 nm). This nanoparticle was obtained by molecular dynamics simulations with a tight-binding atomic potential. The results indicate that in the absence of disorder the level spacing distributions are similar to those expected for systems belonging to the Gaussian Orthogonal Ensemble. Whereas, after increasing the chemical disorder, the electronic level spacing distribution and the Σ_2 statistics tend to the corresponding form for the Poisson Ensemble, i.e., the silver nanoparticle acquires an insulating character which is expected for strongly disordered systems. Hence, this kind of disorder produces the localization of the electronic states of the nanoparticle.

1. Introduction

The development of nanoscience as the XXI century science has allowed the study of a large number of non-traditional systems in condensed matter physics. An example of this kind of systems are the metallic nanoparticles (e.g. silver nanoparticles) which are currently being studied by many research groups [1–7]. The peculiarity of these finite size systems is that they give us the possibility to manufacture electronic devices where electrons can present complex behaviors [8]. Moreover, these systems have a high potential for technological applications in different fields which include electronics, medicine, and biology [9–11].

However, despite the large amount of research on silver nanoparticles, as indicated above, many questions remain unanswered; e.g. the dependence of their physical properties on different parameters, such as the chemical disorder. Previous works have shown that this kind of disorder affects strongly the electronic character of silver and copper nanoparticles [12,13]. These studies were performed by analyzing the nearest electronic level spacing distribution (first neighbors), $P_1(s)$, which is a powerful tool to study electronic properties (short range correlations among electronic levels) of systems with and without disorder [13–21]. For instance, Hofstetter et al. [17], employing a phenomenological formula for $P_1(s)$, have found the critical disorder (W_c) for the three-dimensional Anderson model which evidences the metal–insulator transition in this system. In the same sense, considering concepts of the scaling theory and using other statistics based on $P_1(s)$, Zharekeshev and Kramer [19] determined W_c in three-dimensional systems. Nevertheless, the consequences of disorder on long range correlations among electronic levels of nanoparticles remain poorly understood. In this case, there are two statistical test, Σ_2 and higher electronic level spacing distributions, which give relevant information about these correlations [22,23]. Thus, studies in this direction have been made, e.g., in two-dimensional models of quasicrystals [23–25].

In the context described above, the main aim of this paper is to study the influence of chemical disorder on the electronic level spacing distribution of a silver nanoparticle containing $N=5083$ atoms, Ag_{5083}, (this number belongs to the icosahedral magic numbers sequence [26]), in order to understand the localization phenomenon in this particular system. The nanoparticle is the result of a cooling process at the rate of 0.89 K/ps followed by a relaxation of 1000 ps at 300 K. This process was carried out by molecular dynamics (MD) simulation [27] employing a tight-binding potential [28]. The present article is organized as follows: in Section 2 we present the tight-binding electronic Hamiltonian used to determine the energy spectrum of the nanoparticle. Additionally, we discuss the incorporation of chemical disorder in this system. In the Section 3, we describe the basic concepts of the electronic level spacing distribution. The results and discussion are presented in Section 4. Finally, the conclusions of this study are given in Section 5.

2. Tight-binding electronic Hamiltonian

To calculate the electronic level spacing distribution, we have to determine the eigenvalues $\{E_i\}$ $(i=1,2,\ldots,N)$ of the tight-binding electronic Hamiltonian, H, in similar way as in previous

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works [12,13,29]. This Hamiltonian, in the atomic orbital basis $\{|\vec{R}\rangle\}$ (with a "s" orbital for each atomic site), has the following matrix elements

$$H_{R,R'} = \langle \vec{R}|H|\vec{R'}\rangle = \begin{cases} \varepsilon_R & \text{if } \vec{R} = \vec{R'} \\ t & \text{if } |\vec{R}-\vec{R'}| \le r_c\,, \\ 0 & \text{if } |\vec{R}-\vec{R'}| > r_c \end{cases} \tag{1}$$

with ε_R and $t = 1.0$ eV as the on-site energy and hopping parameter, respectively. We define $r_c = 3.2$ Å as the average distance to nearest neighbors (from a given atom). The atomic positions $\{\vec{R}\}$ are known from the molecular dynamics simulations and fixed to determine the electronic properties. Then, the eigenvalues, $\{E_i\}$, and eigenvectors, $\{|\psi(E_i)\rangle\}$, are obtained from direct diagonalization of the Hamiltonian using Lapack library [30]. In this work, the electronic density of states (EDOS) has been calculated according to the following expression

$$\eta(\xi) = \sum_{i=1}^{N} \delta(\xi - E_i) \approx \sum_{i=1}^{N} \frac{1}{\gamma\sqrt{2\pi}} e^{-(1/2)((\xi - E_i)/\gamma)^2},$$

where γ is the width of the Gaussian function. Besides, the participation ratio (PR) for each eigenvalue is defined by [13]

$$p(E_i) = \frac{1}{N}\left(\sum_{q=1}^{N} |c_q^{(i)}|^4\right)^{-1},$$

with $|\psi(E_i)\rangle = \sum_{q=1}^{N} c_q^{(i)} |\vec{R}_q\rangle$ as the normalized eigenvector corresponding to the eigenvalue E_i. PR presents two limit cases: when $p = 1$ the wave function is fully extended, whereas for $p = 1/N$, it is completely localized [24].

2.1. Chemical disorder

The most effective method for introducing chemical disorder in physical systems is modifying the on-site energy of the Hamiltonian (see Eq. (1)) which can be done employing different kinds of distributions [31]. In the present work, we focus on the box distribution, which consists in uniformly distributing ε_R with random numbers r_R within an energy window W (strength of the disorder), i.e.,

$$\varepsilon_R = r_R / r_R \in \left[-\frac{W}{2}, \frac{W}{2}\right]. \tag{2}$$

The calculations shown in the present work (see Section 4) are averages over 30 random configurations for fixed strength of disorder W.

3. Electronic level spacing distribution

Before calculating any statistical property of the energy spectrum we must first apply an unfolding procedure [16]. Following previous works [12,13,29,32], we will employ a sixth degree polynomial expansion. Then, the energy level spacing is defined by $s_i = e_{i+m} - e_i$ ($m = 1,2,3,4$), where $\{e_i\}$ are the so called unfolded energies [33].

In the context of the electronic level spacing distribution, $P_m(s)$, the distribution for nearest levels (first neighbors), $P_1(s)$, is the most used quantity to study the electronic properties of several complex systems like DNA [14], graphene layers [20,34], quasicrystals [24,33] and nanoparticles [12,13,29]. This is mainly because this distribution has two extreme behaviors with important physical meanings. Namely, in weakly disordered systems (metallic regime) it is known that the level spacing distribution (in units of the average spacing of the nearest levels, $\langle s\rangle_1$) is well described by the Wigner distribution,

$$P_1^W(s) = \frac{\pi}{2} s \exp\left(-\frac{\pi}{4}s^2\right),$$

which is a good approximation to $P_1(s)$ of the Gaussian Orthogonal Ensemble (GOE) from random matrix theory. Whereas in the insulating regime (strongly disordered systems) the level spacing distribution follows a Poisson law [24], i.e.,

$$P_1^P(s) = \exp(-s).$$

Furthermore, for intermediate statistics, between the two limiting cases mentioned above, it has been developed several nearest level spacing distributions. Although none is completely satisfactory from the theoretical point of view, they are employed to evaluate quantitatively the influence of disorder on the electronic properties of a given system. The most used of these intermediate statistics is the Brody distribution [35,36]

$$P_1(s,\beta) = \alpha(\beta+1)s^\beta \exp(-\alpha s^{\beta+1}), \tag{3}$$

with $\alpha = (\Gamma[(\beta+2)/(\beta+1)])^{\beta+1}$ and Γ the well-known Gamma function. This distribution interpolates between the Poisson ($\beta = 0$) and Wigner ($\beta = 1$) ones [16]. Moreover, the statistical parameter β of the Brody distribution is related to the energetic repulsion among levels.

Additionally, in order to study the influence on the long order correlations between the higher electronic levels it is relevant to take attention to distributions corresponding to such spacings (in units of $\langle s\rangle_1$), $P_m(s)$ for $m \ge 2$; which have been studied in very few cases [22,24,25]. In the same sense, we can also study the Σ_2 statistics which measures the fluctuation in the number of energy levels n in an energy range L and it is defined as [16,17]

$$\Sigma_2 = \langle n^2\rangle - \langle n\rangle^2. \tag{4}$$

4. Results and discussion

Structurally, the atomic arrangement of the Ag_{5083} nanoparticle, in a large percentage, is similar to that of its solid counterpart. In fact, this nanoparticle has a noticeable faceted morphology due to its crystallization during the cooling process [13,27]. Thus, its pair correlation function [37], $g(r)$, presents sharp peaks characteristics of this material (see Fig. 1), i.e., the positions of these peaks correspond to those expected in a face centered cubic (fcc) structure [7,13].

Correspondingly, the electronic density of states of this silver nanoparticle and its solid (fcc-like) counterpart are similar [13,38]. These results are in agreement with those found in copper nanoparticles [38]. The participation ratio indicates that the character of the electronic states is constant ($p \sim 0.3$) but complex in almost the whole energy band. Moreover, close to the band edge, the electronic states tend to be localized, i.e., $p \to 1/5083 \sim 0.0002$ (see inset in Fig. 2). In Fig. 3, it can be seen that in absence of disorder the nearest electronic level spacing distribution, $P_1(s)$, is close to the Wigner distribution, which indicates that this system has a metallic character; as was expected since its macroscopic counterpart is a good electrical conductor. Additionally, we found that the nanoparticle presents a Brody parameter $\beta = 0.93 \pm 0.03$, which is close to the value expected in a system that belongs to the GOE ($\beta = 0.95$) [16]. Similar values of β were also found for silver nanoparticles of different sizes obtained by the same formation process [13]. Similar to $P_1(s)$, the higher level distributions, i.e., $P_2(s)$, $P_3(s)$ and $P_4(s)$, are also close to the predictions made, in these particular cases, for systems within the GOE (see Fig. 3). However, these behaviors are different from those expected within the semi-Poisson statistics for systems with multifractal eigenvalues