INVESTIGACIÓN REVISTA MEXICANA DE FÍSICA **45** (4) 342–345 AGOSTO 1999

Metallic behavior of Ni clusters

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Recibido el 22 de junio de 1998; aceptado el 4 de febrero de 1999

We have studied the nonmetal-metal transition in small nickel clusters ($N < 38$) for a large variety of different structures reported in the literature. A self-consistent tight-binding method for the s, p, and d valence electrons in the mean field approximation has been used to calculate the density of states. The prescription employed to identify the nonmetal-metal transition was Kubo's criterion, that establish that the small clusters may remain insulating until the density of states at the Fermi level exceeds $1/(k_{\text{B}}T)$. We compare our results with some experimental results.

Keywords: Nonmetal-metal transition; small Ni clusters

En este trabajo hemos estudiado la transición no metal a metal en cúmulos pequeños de níquel ($N < 38$) para una amplia variedad de estructuras reportadas en la literatura. Un método auto-consitente de amarre fuerte para los electrones de valencia s, p y d en la aproximación de campo medio se utiliza para el cálculo de la densidad de estados. La condición empleada para identificar la transición no metal a metal ha sido el criterio de Kubo, el cual establece que cúmulos pequeños se mantendrán como aislantes hasta que la densidad de estados en el nivel de Fermi excede el factor $1/(k_{\text{B}}T)$. Comparamos nuestros resultados con algunos resultados experimentales.

Descriptores: Transición no metal a metal; cúmulos pequeños de Ni.

PACS: 36.40.Cg; 65.90.+i

1. Introduction

Nowadays, in the case of small cluster sizes, there are many theoretical results in the literature about Ni clusters that provide a great variety of structures, depending on the interatomic potential and on the method used in the calculation, in general these structures are different in sizes and in geometrical shape. A general discussion on the geometrical shape of Ni clusters can be found in Refs. 1–12, and papers quoted therein. However, for small atomic clusters there are other interesting problems regardless of the knowledge of the structure. One of these deals with the metallic behavior of such aggregates, and can be formulated in the following way, what is the cluster size at which the atomic clusters becomes metallic? The understanding of the development of the metallic behavior with increasing particle size has been one of the key questions in the physics of atomic aggregates for many years since it was formulated by Fröhlich more than sixty years ago [13].

A key step to understand the metallic behavior of atomic clusters was first given by Kubo and co-workers [14], who pointed out that a cluster presents metallic behavior when the average spacing between the electronic levels becomes smaller than $k_{\text{B}}T$ and the discrete energy levels begin to form a quasi-continuous band, or formulated in terms of the density of electronic states $\mathcal{D}(E)$: a cluster presents metallic behavior when $\mathcal{D}(E)$ at the Fermi level exceeds $1/(k_{\text{B}}T)$. Although the Kubo criterion is in principle simple to apply, there are many materials for which the critical cluster size is still unknown, that is mainly due to the absence of calculations of $\mathcal{D}(E_F)$ and to the lack of a precise knowledge of the cluster geometry, as it was quoted above.

Recently, it has pointed out that the development of the metallic character of small atomic clusters is driven primarily by the mean coordination number [15]. With the aim to clarify this dependence on the metallic behavior, a theoretical calculation [16] has been carried out within Friedel's model and Kubo's criterion; the main conclusion of this work is that critical cluster size N_c (size at which the cluster develops metallic behavior) for the nonmetal-metal transition is proportional to $\sqrt{Z(N_c)G(T)}$, where $Z(N_c)$ is the average coordination number of an N-atoms cluster at the critical size and $G(T)$ is a function that depends on the temperature and bulk properties of the system. Although the calculation quoted before is based on a very crude approximation for the $\mathcal{D}(E)$ it shows that the nonmetal-metal transition depends mainly on the geometrical structure and particularly on its average coordination number. An excellent review of the experimental and theoretical works on metallic behavior of finite size particles can be found in Ref. 17.

In the case of nickel clusters, and in spite of the partial agreement in the geometrical structures predicted by recent calculations [5–12], some discrepancies exist between them, *e.g.* inter-atomic distance, local coordination number, average magnetic moment, etc. These discrepancies are mainly due to the high number of parameters that have to be taken into account in the calculations, the methods of calculation, and the various types of potentials used to obtain geometrical shapes and electronic properties such as the spin polarized state. The main goal of this work is to find out how these discrepancies modify the metallic character of Ni clusters.

As an attempt to shed some light into the problem of the nonmetal-metal transition in Ni clusters, in this work we performs electronic structure calculations using a tight-binding Hamiltonian for different geometrical structures proposed for Ni clusters in the literature. We use structures calculated by: Nayak *et al.* using a Finnis and Sinclair (FS) many body potential [5], Hu *et al.* using Lennard-Jones (LJ) and Morse (M) pair potentials [6], and López and Jellinek using a Gupta (G) type potential [11]; all these structures has been suggested for Ni clusters based on different energy criterion. Although, the application of the pair potentials (as LJ and M) for metals such as Ni has been criticized, we do not discuss this point here, however the reader can get more details in Refs. 2, 3, 6 and papers quoted therein. The electronic density of states was calculated using a self-consistent tight-binding method, formulated for the $3d$, $4s$, and $4p$ electrons and applying Kubo's criterion to determine the critical cluster size.

In Sect. 2 we describe the theory used in this work, the results are presented in Sect. 3, and a summary and conclusions are given in Sect. 4.

2. Theory

The spin-polarized electronic structure of nickel clusters is determined by solving a self-consistent tight-binding Hamiltonian for the $3d$, $4s$, and $4p$ valence electrons in a mean field approximation. In the usual second quantization notation, this Hamiltonian has the following expression:

$$H = \sum_{i\alpha\sigma} \epsilon_{i\alpha\sigma} n_{i\alpha\sigma} + \sum_{\alpha\beta\sigma_{i\neq j}} t_{ij}^{\alpha\beta} \hat{c}_{i\alpha\sigma}^{\dagger} \hat{c}_{j\beta\sigma} \,, \tag{1}$$

where $\hat{c}_{i\alpha\sigma}^{\dagger}$ ($\hat{c}_{j\alpha\sigma}$) is the creation (annihilation) operator of an electron with spin σ and orbital state α at the atomic site i, and $n_{i\alpha\sigma}$ is the number operator.

The hopping integrals $t_{ij}^{\alpha\beta}$ between orbitals α and β at sites i and j are assumed to be spin-independent and are obtained using the Slater-Koster approximation taking the two-center hopping integrals from Papaconstantopoulos, who fitted them to reproduce the band structure of fcc bulk nickel [18]. The variation of the hopping integrals with the inter-atomic distance r_{ij} is assumed to follow the typical power law $(r_0/r_{ij})^{l+l'+1}$, where r_0 is the bulk equilibrium distance and l, and l' are the orbital angular momenta of the $(i\alpha\sigma)$ and $(j\beta\sigma)$ states involved in the hopping process. The spin-dependent diagonal terms take account for the electron-electron interaction through a correction shift of the energy levels

$$\epsilon_{i\alpha\sigma} = \epsilon_{i\alpha}^{0} + z_{\sigma} \sum_{\beta} \frac{J_{\alpha\beta}}{2} \mu_{i\beta} + \Omega_{i\alpha} \,. \tag{2}$$

Here, $\epsilon_{i\alpha}^{0}$ are the bare orbital energies of paramagnetic bulk Ni. The second term is the correction shift due to the spin-polarization of the electrons at site i ($\mu_{i\beta} = \langle n_{i\beta\uparrow}\rangle - \langle n_{i\beta\downarrow}\rangle$). In this term, $J_{\alpha\beta}$ are the exchange integrals and z_σ is the sign function ($z_\uparrow = 1$, $z_\downarrow = -1$). The exchange integrals involving s and p electrons are neglected and J_{dd} is determined in order to reproduce the bulk magnetic moment [19]. The site- and orbital-dependent self-consistent correction $\Omega_{i\alpha}$ assures the local electronic occupation, fixed in this model by interpolating between the isolated atom and the bulk according to the actual local number of neighbors. The spin-dependent local electronic occupations are self-consistently determined from the local densities of states

$$\langle n_{i\alpha\sigma}\rangle = \int_{-\infty}^{\epsilon_F} \mathcal{D}_{i\alpha\sigma}(\epsilon) d\epsilon \,, \tag{3}$$

which are calculated at each iteration by using the recursion method [20]. In this way, the distribution of the local magnetic moments ($\mu_i = \sum_\alpha \mu_{i\alpha}$) and the average magnetic moment ($\bar{\mu} = \sum_i \mu_i/N$) of Ni_N clusters are obtained at the end of the self-consistent cycle. The total density of states (DOS) at the Fermi level, $\mathcal{D}_N(E_F) = \sum_{i\alpha\sigma} \mathcal{D}_{i\alpha\sigma}(E_F)$ results also from the self consistent calculation and we have used it to determine the nonmetal-metal transition according to the Kubo criterion [14], that is $\mathcal{D}_N(E_F) \geq 1/k_{\mathrm{B}}T$ for the development of metallic behavior.

This one particle Hamiltonian neglects correlation effects beyond the mean field approximation and the dependence of the DOS with the temperature. This assumption seems to be adequate since previous calculations at finite temperature including correlations effects for bulk Ni [21] demonstrate that the DOS does not change appreciable near the Fermi energy for temperatures lower than 640 K: The Fermi energy always lies on a pronounced peak characteristic of the *fcc* structure. Therefore, changes in the DOS are expected to occur only as a consequence of the finite size and geometry of the clusters. It is also important to mention that it is assuming that there are not structural transitions in the temperature range here considered.

3. Results

Considering that the number of electrons that contributes to establish the metallic behavior is proportional to the number of atoms N in the aggregate and that such dependence might hide some effects, we show in Fig. 1 the normalized DOS at the Fermi level, that is $\mathcal{D}_N(E_F)/N$. The geometries used in the calculation are those calculated by Nayak *et al.* [5] (represented by • in the figure) who had calculated them using a semi-empirical pair potential developed by Finnis and Sinclair (FS) based on tight-binding total energy calculations and containing many-body terms. A second set of geometries in this work are those calculated by Hu and co-workers [6], these structures had been obtained combining molecular dynamics and Monte-Carlo method with a Lennard-Jones ($*$) and Morse ($\times$) pair potentials. A third set of geometries are those calculated by López and Jellinek from molecular dynamics simulations with a Gupta type potential ($\triangle$) [11].

TABLE I. The five different structures for clusters with $N = 8$ that shows different results obtained using different parameters, methods and potentials. Structure with (•) symbol corresponds to Ref. 5 obtained by molecular dynamics. Those quoted with (⋆) and (×) were obtained by Monte-Carlo method, respectively [6]. Symbol (♦) is a proposed structure by Parks and co-workers [22] from experimental work. Structure quoted by (△) was obtained using molecular dynamics [11]. See specific references for details.

Identified structure (Potential)	$n_i(Z_i)$	$\bar{Z}$	d_n(Å)
•Bicapped octahedral (Finnis and Sinclair) [5]	4(4), 4(5)	4.5	2.25
⋆Capped pentagonal bipyramid (Lennard-Jones) [6]	1(3),3(4),2(5),1(6),1(7)	4.75	2.48
×Deformed central tetrahedron (Morse) [6]	4(4), 4(6)	5.0	2.48
△Bicapped octahedral (Gupta) [11]	4(4), 4(5)	4.5	2.46
♦Saturated tetrahedron (Suggested by the experiment) [22]	4(3), 4(6)	4.5	2.43

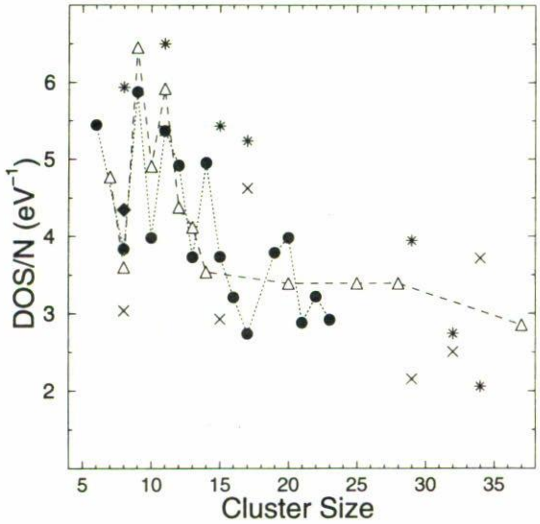

FIGURE 1. Normalized density of states at the Fermi level as a function of the cluster size. The sharply and oscillatory behavior that all the systems show, specially at small size clusters, reflects the strong dependence of the $[\mathcal{D}(E_F)/N]$ with the geometrical structure in this range. Here, (•) corresponds to structures calculated with Finnis and Sinclair type potential [5], (∗) and (×) are geometries obtained with Lennard-Jones and Morse pair potentials respectively, while the (♦) is a structure proposed by Riley *et al.* in Ref. 22. The triangles (△) correspond to structures by López and Jellinek [11], using a Gupta type potential.

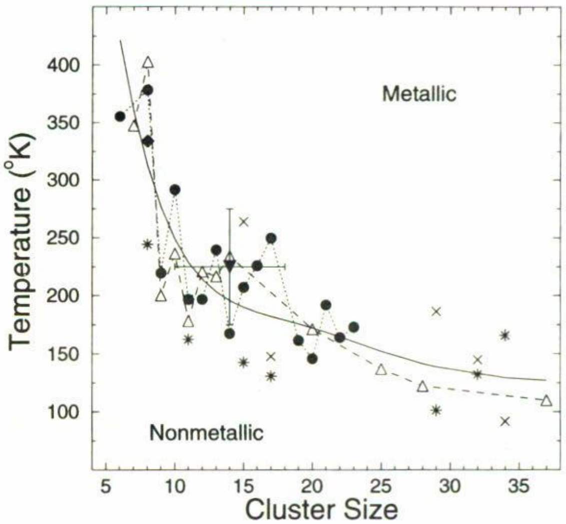

FIGURE 2. Plot of the nonmetal-metal phase diagram calculated for Ni clusters in this work. The continuous line is a guide to the eye for the nonmetal-metal transition. The points below this line could be considered as non-metallic clusters, whereas those above the line present metallic behavior. The black triangle (▾) is derived from a ionization potential measurement by the experimental results by Parks *et al.* [25].

As an example of the discrepancies in the geometrical shapes of the clusters and others problems mentioned in the introduction, consider for instance the different clusters proposed for Ni_8 in Fig. 1; the different geometrical properties are summarized in Table I. All the structures are different among themselves, *e.g.*, if two of them (FS and G) have the same structure, they have different inter-atomic distance (d_n), or if they have the same coordination number (Z) (FS and M), they differ by the structure, and so on. Such discrepancies are reflected in the electronic properties of these systems. This can be observed in the normalized density of states $[\mathcal{D}_N(E_F)/N]$ shown in Fig. 1, and in the phase diagram of nonmetal-metal behavior at Fig. 2 (T *vs.* N), where we have applied the Kubo's criterion to study the metallic behavior. In Fig. 1, we observe in general an overall decreasing in the $[\mathcal{D}_N(E_F)/N]$ as a function of the cluster size for all the different geometries here considered. The normalized density of states shows an oscillatory behavior for small N, that clearly reflects strong dependence on the geometry and is not easy to explain in simple terms. It is related to the detailed changes of the structure and inter-atomic distance with N. In particular, we notice that the $[\mathcal{D}_N(E_F)/N]$ for the clusters based on the Morse (×) potential is the one that presents the most complex behavior.

Figure 2 shows the main result of this work: the phase diagram for the nonmetal-metal transition. The solid-line is just an aid to the eye to visualize the boundary of the nonmetal-metal transition. The region below the boundary describes non-metallic clusters while the region above corresponds to the metallic state for atomic clusters. The boundary becomes steep and irregular for small size clusters, whereas for larger cluster sizes the boundary becomes less irregular with a slope that decreases continuously as the cluster size increases. Using the solid line as a guide we can conclude that at room temperature Ni clusters larger than 10 atoms present metallic behavior, whereas at liquid nitrogen (77 K) temperature there are required at least 50 atoms to get the metallic behavior in atomic clusters.

We are not aware of any direct experimental measurement of the nonmetal-metal transition in Ni clusters, since most of the experimental results are for Pd, Fe, Hg, Ag, Au, Cu, etc. clusters [17]. However, based on measurements of the ionization potential (IP) one can estimate the critical cluster size for the nonmetal-metal transition [16, 23]. It is well known that the metallic behavior in large clusters implies that the size variation of the IP satisfies the equation [24]

$$\mathrm{IP}(N) = \mathrm{IP}_0 + CN^{-1/3}\,, \tag{4}$$

where IP_0 is the bulk work function (ionization potential of the macroscopic metal) and C is a constant (the asymptotic slope in a plot for large size clusters). In the case of small aggregates a linear fit in $N^{-1/3}$ also often works, although the slope and the constant term are different. It can be estimated the nonmetal-metal transition as a function of the cluster size where the two linear fits intercept, since this is the size at which Eq. (4) starts to hold. The result of this estimation using the ionization potentials measured by Parks [25] is included in Fig. 2 as a black triangle (▼), with error bars indicating the experimental uncertainty. Considering this experimental result, we obtain a fairly agreement with our work.

4. Conclusions and summary

We have studied the nonmetal-metal transition in Ni clusters for some of the different geometrical shapes proposed in the literature. A self-consistent tight-binding method for the s, p, and d valence electrons has been used to calculate the electronic density of states (DOS). The Kubo's criterion was applied to identify the nonmetal-metal transition in atomic clusters. Metallic behavior in atomic clusters is presented for Ni clusters with 10 atoms at room temperature and with more than 50 atoms at temperature of 77 K (liquid nitrogen). We compare our calculations with Park's experimental results and we found a good agreement.

Acknowledgments

We acknowledge to Prof. P. Jena and Dr. S.K. Nayak, and Dr. W.J. Hu, for give us their cluster coordinates and let us use them in this study. J.L.R.L. acknowledged scholarship support from CONACyT. This work is partially supported by CONACyT, México under Grant 25851-E. We are also greatful acknowledged to Dr. A. Vega, Dr. J.M. Montejano-Carrizales, and M.C. Báez for his comments and suggestions to the manuscript.

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