Available online at www.sciencedirect.com

SCIENCE DIRECT

Physica B 354 (2004) 278–281

PHYSICA B

www.elsevier.com/locate/physb

Magnetism in segregated bimetallic CoRh nanoclusters

E.O. Berlanga-Ramírez[a,*], F. Aguilera-Granja[a], J.M. Montejano-Carrizales[a], A. Díaz-Ortiz[b], K. Michaelian[c], A. Vega[d]

[a]Instituto de Física, Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, SLP, Mexico
[b]Centro Nacional de Supercómputo, IPICyT, Apartado Postal 3-74 Tangamanga, 78231 San Luis Potosí, SLP, Mexico
[c]Instituto de Física, Universidad Nacional Autónoma de México. 20-364, 01000 DF, Mexico
[d]Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, E-47011 Valladolid, Spain

---

Abstract

The magnetic properties of free-standing Co_nRh_m clusters ($N = n + m \approx 110$ and $n \approx m$) of three different symmetries: cubo-octahedral, icosahedral and HCP, were investigated in the segregated case. The initial geometrical structures constructed at Rh bulk distances were relaxed with a many-body Gupta potential to obtain the cluster geometries and energies. We find that the lowest energy is associated with the HCP structure. The relaxed interatomic distance for all the structures is slightly lower than the Rh bulk distance. The spin-polarized electronic structure and related magnetic properties of these optimized geometries were calculated by solving self-consistently a spd tight-binding Hamiltonian. The magnetic moment of the Rh atoms shows strong dependence on the position and environment, whereas the Co atoms show a smoother dependence. Results are compared with the experimental data and with other theoretical calculations available in the literature.

PACS: 36.40.Cg; 75.50.−y; 61.46.+w

Keywords: Magnetic nanostructures; Transition-metal clusters; Electronic properties; Tight-binding methods

---

1. Introduction

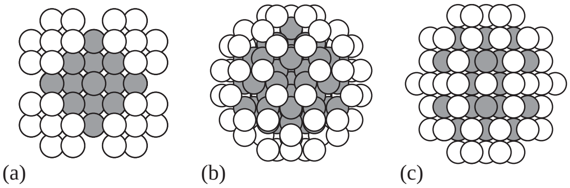
A big challenge in the material science is to combine the finite size effects present in the nanosystems with the multicomponent character of the alloys with the aim to find novel properties not present in bulk systems of both pure and mixed materials. In order to find out the role of the superposition of both effects very recently bimetallic clusters of 3d and 4d particles were synthesized, e.g. CoRh and NiPd. Motivated by the previous experimental results in this work we study the magnetic behaviour of CoRh nanoparticles with three different types of geometrical

---

[*] Corresponding author.
E-mail address: berlanga@dec1.ifisica.uaslp.mx (E.O. Berlanga-Ramírez).

0921-4526/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2004.09.063

structures presenting segregated chemical order. There are only few theoretical works in the literature considering this problem, being most of them at very small sizes and only a few of them lies in the nanometer size range. To determine the role of the structure and bond size in the magnetic properties of bimetallic Co–Rh clusters, we locally optimized some of the possible structures quoted by the experimentalists [1] such as icosahedral, FCC and HCP using a semi-empirical Gupta potential. For these relaxed structures, we determined the electronic properties using a parameterized tight-binding (TB) Hamiltonian in the mean field approximation for spd valence electrons of Co and Rh. The same model has been used in our previous studies of small pure Co and Rh clusters [2,3]. In the following sections, we present the theoretical models and approximations used for the geometric and electronic parts of the problem. Next, we discuss the results and compare them with the experiment and available theoretical results. Finally, we present a summary and conclusions.



	Segregated					
	$\bar{\mu}_{\mathrm{Rh}}$	$\bar{\mu}_{\mathrm{Co}}$	$\bar{\mu}$	E (eV/at)	x_{Co}	$\bar{\mu}_{\mathrm{Rh}}/\bar{\mu}_{\mathrm{Co}}$
(a) Cubo	0.27	2.44	1.36	−4.184	0.504	0.11
(b) Ico	0.19	2.45	1.37	−4.145	0.521	0.08
(c) hcp	0.34	2.28	1.44	−4.328	0.565	0.15

Fig. 1. Illustration of the cluster geometries obtained from the local optimization, where the white spheres represent the cobalt atoms and the gray ones corresponds to rhodium atoms. The three types of different structures are: (a) Cubo-octahedral cluster $N = 111$, (b) Icosahedral cluster $N = 115$, and (c) Hexagonal close-packing cluster $N = 115$. Below the geometries are given the average values of the magnetic moments for the two components, $\bar{\mu}_{\mathrm{Rh}}$ and $\bar{\mu}_{\mathrm{Co}}$, for the different clusters, cohesive energy per atom, the Co concentration, x_{Co}, and the ratio of the average Rh magnetic moment to the average Co magnetic moment $R = (\bar{\mu}_{\mathrm{Rh}}/\bar{\mu}_{\mathrm{Co}})$.

2. Geometrical model and approximations

For the initial cluster geometries we assumed three different possible structures; (i) FCC truncated cuboctahedral growth $N = 111$, (ii) truncated icosahedral $N = 115$, and (iii) HCP fragment $N = 115$. The initial nearest-neighbour (NN) distance, in units of the Rh-bulk value (2.69 Å), between the atoms in the clusters was set equal to 1.0 for the FCC and the HCP and to an average of 1.03 for the icosahedral due to the two types of interatomic distances within this cluster. In all cases, we fixed the composition as close as possible to the equiatomic concentration ($\mathrm{Co}_n\mathrm{Rh}_m$ with $n \approx m$) keeping the symmetry of equivalent sites. For the sake of simplicity in this paper, we restricted ourselves to the segregated chemical order; however, the possibility that other type of chemical order may be present cannot be ruled out. As suggested by the experimental report, we considered a Rh closed shell core surrounded by Co layers. The geometrical shapes of the clusters used in this work facilitated the comparison of the effect of geometry on the magnetic character since the systems are constructed of approximately the same number of atoms. The cluster energies and optimized geometries were obtained by performing local conjugate gradient relaxations using an all atom, n-body Gupta potential modelling the interatomic interactions (see Refs. [2–5] for details). The geometrical shapes of the clusters resulting from the optimization are illustrated in Fig. 1.

3. Electronic model and approximations

The spin-polarized electronic structure of CoRh clusters was determined by solving self-consistently [6] a TB Hamiltonian for the 3d, 4s and 4p valence electrons for the cobalt atoms, and 4d, 5s, and 5p for the rhodium atoms. Calculations are done in the mean-field approximation. The hopping integrals were determined by fitting to the band structure of both Co and Rh bulks [7]. The exchange integrals involving s and p electrons were neglected taking into account only the integral corresponding to d electrons (J_{dd}). Since rhodium bulk metal is paramagnetic, we have taken $J_{dd} = 0.40\,\mathrm{eV}$ so that it reproduces the magnetic moments of the Rh_{13} as predicted by first-principles density functional calculations [8]. In the case of cobalt, the $J_{dd} = 1.44\,\mathrm{eV}$ was fitted in such a way that it reproduces the bulk magnetic moment [9]. The description of the magnetic properties of low-dimensional 4d transition metal systems requires the same ingredients as for the 3d series, in particular, the explicit consideration of the electronic delocalization in order to account for the itinerant character of the magnetism of these materials and also the symmetry of each system which plays an important role due to the directional bonding. The fact that this TB model has been successfully applied to the study of pure Co and Rh clusters [2,3] give us confidence in its utilization for the mixed clusters [5].

4. Results and discussion

We first discuss the details of the optimized geometrical structures. In the upper panel of Fig. 1, we present a view of the investigated clusters. We assume three different possible structures: (i) cubo-octahedral growth (FCC) $N = 111$, (ii) icosahedral $N = 115$, and (iii) HCP $N = 115$ with segregated chemical order and initial neighbour distance equal to the Rh bulk value. These clusters consist of a Rh rich core surrounded by Co shells. In general after the relaxation, the average bond length in the different clusters slightly shrinks ($\sim$2%) with respect to the Rh bulk value as expected due to the finite size of the system [2,3]. This relaxation shows a non-uniform compression depending on the position and on the type of atoms. The largest shrinking is presented for the icosahedral shape ($\approx$3%), followed by the cubo-octahedral ($\approx$1.5%), and finally the HCP ($\approx$1%). These small compressions are reasonable considering that previous semi-empirical global optimization for pure Rh and Co clusters indicates that the interatomic distances reach the bulk values for relative small sizes [2,3]. The bond distribution within the clusters is as follows: approximately 45% of the first nearest neighbours pairs (FNNP) are Rh–Rh, 30% corresponds to Rh–Co FNNP, and 25% are Co–Co type. In our model, the HCP structure is the one with the lowest energy (see Fig. 1) followed by the cubo-octahedral and the icosahedral, respectively. It is important to note that the experiment of Zitoun et al. [1] suggested that the lowest energy structure may be the icosahedral with a uniform Co–Rh distribution.

In our cluster geometries, the magnetic moments of the Rh atoms at the Co–Rh interface are in the range of 0.2–$1.0\mu_B$. In general, the magnetic moment increases as we move away from the centre of the cluster. At the interface, the larger numbér of Co atoms around a Rh site induces an enhancement of the magnetization in Rh sites. On the other hand, at the surface, the low coordination is associated with the high magnetic moment of the Co atoms. Both effects work in the same direction of increasing the magnetic moment of the cluster, which is otherwise slightly reduced due to the antiferromagnetic alignment at part of the Rh core. An analysis of the local magnetic properties allows an understanding of the experimentally measurable average magnetic moments (AMM-s). In the lower panel of Fig. 1, we show the AMM per Rh atoms ($\bar{\mu}_{Rh}$), per Co atoms ($\bar{\mu}_{Co}$), the AMM within the cluster ($\bar{\mu}$), the cohesive energy per atom E, the Co concentration x_{Co}, and the ratio of the average Rh magnetic moment to the average Co magnetic moment $R = (\bar{\mu}_{Rh}/\bar{\mu}_{Co})$ for the different structures. In a previous theoretical calculations, Dennler et al. [10] reported a ratio R in the range of 0.43–0.53 within the framework of DFT–GGA for Co_2Rh_2 microclusters; Sondón et al. [11] using a TB approximation obtained $R \approx 0.6$ for a Co–Rh icosahedral cluster with 55 atoms; and finally in the bulk limit for a binary HCP Co–Rh systems Moraitis et al. [12] obtained $R \approx 0.16$ using a TB linear muffin-tin orbital. Experimental investigations in Co–Rh thin film alloys by Harp et al. [13] at room temperature give 0.25 for this ratio. In the present work this ratio goes from 0.08 to 0.15 (with an average value of 0.11). All the results for $R = (\bar{\mu}_{Rh}/\bar{\mu}_{Co})$ indicate that in general this ratio increases respect to the bulk value [12] when the size of the system is reduced. The value of R also depends mainly on the concentration of the components and on the kind of chemical order presented within the clusters. However, the only way to see a fair comparison between the different methods and approximations, is to perform the calculation of R for a fixed size cluster with a given composition and chemical order.

The magnetic moments reported experimentally by Zitoun et al. [1] in Co–Rh clusters ($N = 220$), assuming a homogeneous system and the bulk theoretical ratio of Moraitis et al. [12], are $\mu_{\mathrm{Co}} = 2.02\mu_{\mathrm{B}}$ and $\mu_{\mathrm{Rh}} = 0.32\mu_{\mathrm{B}}$. For our most stable configuration (HCP), we obtain $\mu_{\mathrm{Co}} = 2.28\mu_{\mathrm{B}}$ and $\mu_{\mathrm{Rh}} = 0.34\mu_{\mathrm{B}}$. Sondón et al. [11], for the icosahedral cluster ($N = 55$) give $2.02\mu_{\mathrm{B}}$ for Co and $1.23\mu_{\mathrm{B}}$ for Rh, respectively. Based on the previously discussed results, the bulk ratio $\mu_{\mathrm{Rh}}/\mu_{\mathrm{Co}}$ used in the interpretation of the experimental results may not be adequate for these finite systems and in that case, the proposed experimental values would be slightly modified when a theory for finite size system is used. Interpretation of the experimental results should consider that this ratio depends on the system size, as well as on the chemical order.

5. Summary and conclusions

We studied the magnetic properties of free-standing $\mathrm{Co}_n\mathrm{Rh}_m$ segregated clusters ($N = n + m \approx 110$ and $n \approx m$) with three different symmetries: cubo-octahedral, icosahedral and HCP. The optimization results indicate that the interatomic distance for all the structures slightly decreases (~2%), in good agreement with the experiment. We find that the lowest-energy structure is the HCP. Since theoretical calculations [11] suggest that small Co–Rh clusters ($N \leqslant 55$) prefer the icosahedral structures, whereas bulk like systems form a HCP solid [14], it is expected that a structural transition takes place at some intermediate size. From our calculations, this structural transition may be located at sizes in the range of hundreds of atoms. For all the clusters studied here the magnetic moment of the Rh atoms shows a strong dependence on the geometrical environment. Finally, from our results, as well as from other theoretical calculations [10–12], it is found that the ratio $R = (\bar{\mu}_{\mathrm{Rh}}/\bar{\mu}_{\mathrm{Co}})$ depends on the size of the system and on the local geometrical properties.

Acknowledgements

This work was partially funded by CONACyT (Mexico) (39577-F and 40393-A), PROMEP-SEP-CA230, and DGAPA-UNAM IN-104402. Financial support from MCyT (Spain) MAT2002 04393 C02 01, and from the Junta de Castilla-León VA 073/02 is gratefully acknowledged. FA-G acknowledges the partial support of CONACyT-2004. Finally, EOB-R thanks the Ph.D. Fellowship Program of CONACyT.

References

[1] D. Zitoun, M. Respaud, M.C. Fromen, M.J. Casanove, P. Lecante, C. Amiens, B. Chaudret, Phys. Rev. Lett. 89 (2002) 037203.
[2] J.L. Rodríguez-López, F. Aguilera-Granja, K. Michaelian, A. Vega, Phys. Rev. B 67 (2003) 174413.
[3] F. Aguilera-Granja, J.L. Rodríguez-López, K. Michaelian, E.O. Berlanga-Ramírez, A. Vega, Phys. Rev. B 66 (2002) 224410.
[4] K. Michaelian, N. Rendón, I.L. Garzón, Phys. Rev. B 60 (1999) 2000.
[5] E.O. Berlanga-Ramírez, F. Aguilera-Granja, J.M. Montejano-Carrizales, A.Díaz-Ortiz, K. Michaelian, A. Vega, Phys. Rev. B 70 (2004) 014410.
[6] R. Haydock, in: E. Ehrenreich, F. Seitz, D. Turnbull (Eds.)., Solid State Physics, vol. 35, Academic Press, London, 1980, p. 215.
[7] D.A. Papaconstantopoulos, Handbook of the Band Structure of Elemental Solids, Plenum, New York, 1986.
[8] Y. Jinlong, F. Toigo, W. Kelin, Phys. Rev. B 50 (1994) 7915.
[9] C. Kittel, Introduction to Solid State Physics, seventh ed., Wiley, New York, 1996.
[10] S. Dennler, J.L. Ricardo-Chavez, J. Morillo, G.M. Pastor, Eur. Phys. J. D 24 (2003) 237.
[11] T. Sondón, M.Sc. Thesis, Comisión Nacional de Energía Atómica, 2003;
Private communication with J. Guevara.
[12] G. Moraïtis, H. Dreysse, M.A. Khan, Phys. Rev. B 54 (1996) 7140.
[13] G.R. Harp, S.S.P. Parkin, W.L. O'Brien, B.P. Tonner, Phys. Rev. B 51 (1995) 12037.
[14] W. Koster, E. Horn, Z. Metallkd. 43 (1952) 444.