

Magnetic structure of small Fe-Ni clusters: calculations in the Ni rich region

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Small clusters present many novel properties absent in bulk materials. One of the most relevant features of small transition metal systems is their magnetic behavior. Monoatomic clusters show a magnetic moment per atom larger than the in the bulk. However, Fe-Ni clusters have experimentally a lower magnetization than the corresponding bulk alloy values. In this contribution we calculate electronic and magnetic structure of $\text{Fe}_{1-x}\text{Ni}_x$ clusters, for $x > 0.5$. We find ferro- and antiferromagnetic self-consistent solutions, in the antiferro solutions the Fe atoms are antiferromagnetically aligned among themselves, while the Ni atoms have a lower local magnetization than in the bulk.

Keywords: Mixed clusters; magnetism

Agregados de pocos átomos presentan propiedades distintas a las de volumen. Una de las características relevantes de los agregados de metales de transición es su comportamiento magnético. Los agregados de un sólo tipo de átomo tienen un momento magnético por átomo mayor que en el volumen. Sin embargo agregados de Fe-Ni presentan experimentalmente un momento menor que la aleación. En esta contribución calculamos la estructura electrónica y magnética de agregados $\text{Fe}_{1-x}\text{Ni}_x$, para $x < 0.5$. Encontramos soluciones autoconsistentes ferro y antiferromagnéticas. En las antiferromagnéticas los átomos de Fe se polarizan antiferro, mientras que los átomos de Ni presentan una magnetización local menor que la de volumen.

Descriptores: Cúmulos mezclados; magnetismo

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1. Introduction

Ultrafine particles (UFP) have magnetic and electronic properties different from those of bulk materials. Their magnetism is considered to be of singular importance for magnetic recording applications. From the technological point of view it is convenient to have very small particle sizes, since magnetic recording density, recording speed, noise suppression and lifetime are enhanced in this way. The most widely used magnetic materials are Fe-Ni alloys which are known to present anomalies in their physical properties, such as Invar and Permalloy (in the Fe-rich region).

Recently Li *et al.* [1] have experimentally investigated Fe-Ni UFP over a wide range of composition. When the Fe content is less than 60 at.% the structure of the samples is *fcc*, and for increasing amount of Fe the *bcc* phase appears. The authors have found that the saturation magnetization of these UFP decreases significantly as compared with the corresponding Fe-Ni bulk alloys.

In previous works we have shown that Fe clusters in the *fcc* structure have many magnetic self-consistent solutions [2] most of them antiferromagnetic (AF). In this contribution we try to explain the experimental decrease in the UFP magnetization by doing calculations in the Ni rich region of Fe-Ni particles.

2. Method for cluster calculations

A tight-binding Hamiltonian with *s*, *p*, and *d* orbitals and parameters taken from the corresponding bulk materials is used for the cluster calculations. Magnetism is obtained from a Hubbard-like term solved in the unrestricted Hartree-Fock approximation and only nearest neighbor two center parameters are considered. All many-body contributions appear in the diagonal term, $\epsilon_{im\sigma}$, and are given by

$$\epsilon_{im\sigma} = \epsilon_{im}^0 + \sum_{m'} U_{imm'} \Delta\eta_{im'} - \sigma \sum_{m'} \frac{J_{imm'}}{2} \mu_{im'} + \Delta\epsilon_i^{\text{MAD}} \quad (1)$$

where $\Delta\eta_{im'}$ is the electronic occupation difference per orbital in the *i*-th atom of the cluster with respect to the bulk paramagnetic values, $\mu_{im'}$ is the magnetization per orbital and $\Delta\epsilon_i^{\text{MAD}}$ is the Madelung term. The single-site energies ϵ_{im}^0 and the hopping elements of the Hamiltonian are taken to be equal to the bulk values obtained from Andersen's canonical LMTO-ASA paramagnetic bands [3]. The hopping parameters are assumed to be always spin independent and the

heteronuclear ones at the Fe-Ni interfaces are averaged as in Ref. 4. $U_{imm'}$ are the screened intrasite Coulomb integrals in the solid. The values U_{idd} are obtained using our bulk occupations following Ref. 5 and the U_{iss}/U_{idd} relations are taken from atomic tables. $J_{imm'}$ are the intrasite exchange integrals and are assumed to be zero except for d orbitals. J_{idd} is fitted to obtain experimental bulk magnetizations.

The Madelung term, $\Delta\epsilon_i^{\text{MAD}}$, must be added because of the presence of large charge transfers among shells within the clusters. It consists of the sum of electrostatic potentials over all cluster sites

$$\Delta\epsilon_i^{\text{MAD}} = \sum_{l \neq i} V_{il} \quad (2)$$

where V_{il} contains the interatomic electrostatic interactions between atoms on sites \mathbf{R}_i and \mathbf{R}_l . For a bulk parametrization an expression commonly used in alloys and multilayers as in Ref. 6 is appropriate,

$$V_{il} = \frac{U}{1 + U|\mathbf{R}_i - \mathbf{R}_l|} \Delta\eta_l \quad (3)$$

where $\Delta\eta_l$ is the total electronic occupation difference with respect to the paramagnetic bulk values on the l -th atom of the cluster. Taking into account that in late transition metals there are more d than sp electrons, we have taken for U the average of the Fe and Ni values for d orbitals.

Extra orbitals s' outside the clusters are added to account for electron spill over at the surface and we parametrize them in order to get adequate d orbital occupations. The selection of the s' -orbital site energy is related to the average coordination of the surface atoms. The number of s' orbitals added is such that each cluster atom keeps its bulk coordination. The s' -orbital site energies for Ni and Fe are the same so that in this case we have only one more parameter introduced by the s' -orbitals, as when dealing with homonuclear clusters. [2]

In order to compare among different magnetic configurations the following expression for the cluster band energy contribution is used,

$$E_T = \sum_j E_j^T - U_e \quad (4)$$

the summation is done up to the Fermi energy, U_e is the correction introduced to avoid double counting of electron repulsion,

$$U_e = \sum_{im\sigma} \frac{1}{2} \eta_{im\sigma} (\epsilon_{im\sigma} - \epsilon_{im}^0) \quad (5)$$

3. Results and discussion

We show here the results obtained for a cluster of 225 atoms ($N = 225$), that is, 47 Fe atoms and 178 Ni atoms. This system is in the Ni-rich region, near to the $\text{Fe}_{25}\text{Ni}_{75}$ composition. We obtain many different self-consistent magnetic solutions. The cluster has 12 atomic shells, the Fe atoms build all the odd numbered shells (being the first one the central

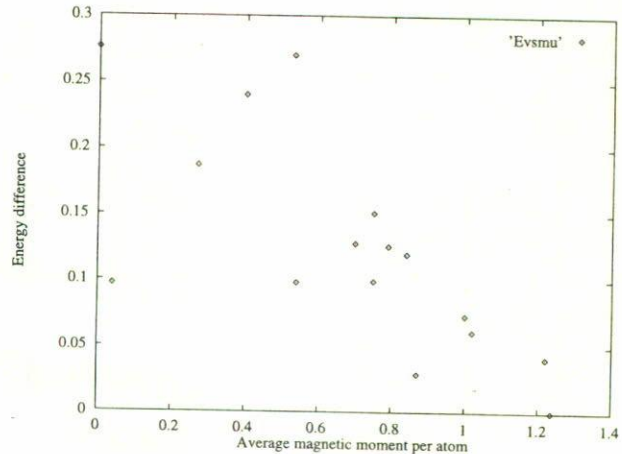


FIGURE 1. Energy difference per atom with respect to the most stable solution, ΔE , for different magnetic configurations versus average magnetic moment. The data correspond to a cluster of 47 Fe and 178 Ni atoms. Energies in eV and magnetic moments in μ_B .

atom) and the rest of the shells are Ni only ones. The most stable solution, within our approximation, is the ferromagnetic one, with an average magnetic moment per atom of $1.25 \mu_B$. This value is slightly larger than that corresponding to the bulk alloy. The Ni local magnetic moments are close to the bulk value, but Fe atoms show a clear surface effect with an increased magnetization in the outer shells. Nearest in energy to this F solution lies one with $0.87 \mu_B$ per atom. In this solution the first and the seventh shells are AF with respect to the rest, and the Ni atoms have a lower magnetic moment than in the bulk. The absolute values of the local magnetic moments of the Fe atoms are similar in both the F and AF configurations.

In Fig. 1 we plot the energy difference per atom with respect to the most stable solution (F), ΔE , for many possible self-consistent magnetic structures versus the average magnetic moment per atom. The very low experimental values obtained by Li *et al.* [1] for the magnetization of the Fe-Ni particles could be attributed, according to our results, to the existence of AF configurations very near in energy to the F one.

In Figures 2 and 3 we show the local magnetic moment per atom for the two most stable magnetic configurations versus shell number (see Fig. 1). It is seen that the outer Fe atoms show a magnetic enhancement due to surface effects. Ni atoms do not have a larger magnetization than in the bulk, as it is seen in homonuclear Ni clusters, [2] this is due to the existence of charge transfer from Fe to Ni. In the AF configuration the last shell, which is a Ni one, is magnetically dead. The existence of many AF magnetic solutions, very near in energy, is a clear outcome of this study and can explain the reported experimental results. Our calculations are not total energy ones and one has to be cautious about energy differences. Anyway, it would be hard with the computational facilities available nowadays to treat clusters of more than 50 atoms, that show so many magnetic self-consistent solutions, using *ab initio* methods. For the cluster considered in

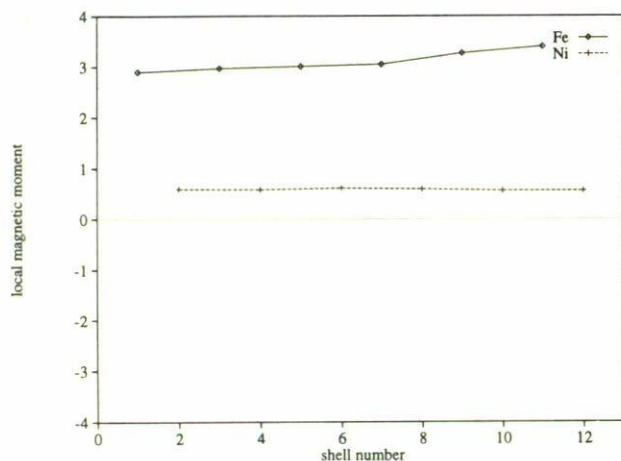


FIGURE 2. Local magnetic moment per atom (in μ_B) versus shell number for the cluster of 225 atoms in the F configuration. (\diamond) corresponds to Fe atoms and (+) to Ni.

this contribution no kind of segregation was taken into account. This effect could lead to Fe accumulation in *fcc* structure, and therefore to an even larger decrease of the total magnetization of the system. Both effects then, the existence of AF solutions and disorder, could explain the experimental low magnetizations.

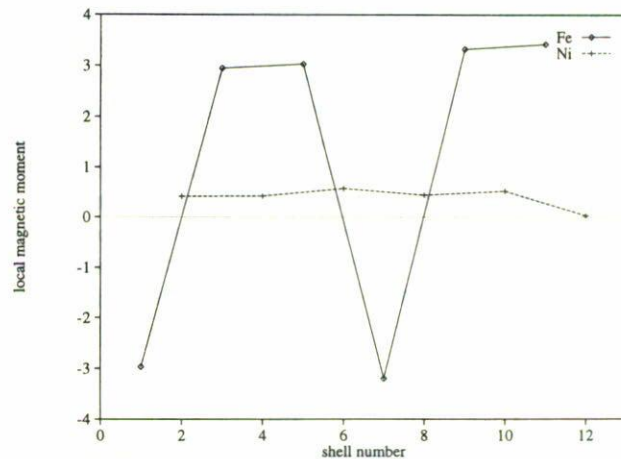


FIGURE 3. *Idem* Fig. 2 but for the AF configuration of lowest energy.

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1. X.G. Li, A. Chiba, and S. Takahashi, *J. Magn. Magn. Mater.* **170** (1997) 339.
2. J. Guevara, F. Parisi, A.M. Llois, and M. Weissmann, *Phys. Rev. B* **55** (1997) 15289; *ibid Computational Materials Science* (in press).
3. O.K. Andersen and O. Jepsen, *Phys. Rev. Lett.* **53** (1984) 2471; O.K. Andersen, O. Jepsen, and D. Gloetzel, in *Highlights of*

Condensed Matter Theory, edited by F. Bassani, F. Fumi, and M. Tosi, (North Holland, Amsterdam, 1985)

4. H. Shiba, *Prog. Theor. Phys.* **46** (1971) 77.
5. T. Bandyopadhyay and D.D. Sarma, *Phys. Rev. B* **39** (1989) 3517.
6. G. Fabricius, A.M. LLois, M. Weissmann, and M.A. Khan, *Phys. Rev. B* **49** (1994) 2121; G. Fabricius, A.M. Llois, and M. Weissmann, *ibid.* **44** (1991) 6870.