

Spin and orbital moments of Fe clusters supported on Ni(001)

R Robles^{1‡}, A Bergman¹, A B Klautau², O Eriksson¹ and L Nordström¹

¹ Department of Physics, Uppsala University, Box 530, SE-75121 Uppsala, Sweden

² Departamento de Física, Universidade Federal do Pará, Belém, PA, Brazil

Abstract. The spin and orbital moments for small Fe clusters deposited on a Ni(001) surface have been calculated by means of an *ab initio* method. We find enhanced spin and orbital moments compared to what is found in bulk Fe. Our obtained spin moments are in good agreement with previous theoretical studies on similar systems. Comparing our results with a recent x-ray magnetic circular dichroism study [J. T. Lau *et al* 2002 *Phys. Rev. Lett.* **89** 057201], we find that the calculated orbital moments are much lower than the experimentally found. Reasons for this discrepancy are discussed.

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‡ Present address: Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000, USA

1. Introduction

Magnetic nanostructures in form of small clusters deposited on a metal surface have recently attracted considerable attention. Due to their size and confinement to the surface, these clusters often have magnetic properties different from what is found in bulk material. Usually, the atoms in these small clusters exhibit enhanced magnetic moments, which can be explained by band narrowing that is caused by the lowered coordination for the cluster atoms. Due to the reduced symmetry, the orbital moments are often enhanced as well, which can result in large anisotropies for supported clusters [1]. These properties are desired for industrial applications e.g. in future data storage applications [2]. Another interesting feature of supported clusters is that by increasing the cluster size, it is possible to monitor the change of the magnetic properties as the studied systems vary from atomic-like to a fully bulk-like behaviour.

The interest in this field is also fuelled by recent advances in experimental techniques, like spin-polarised scanning tunnelling microscopy [3] and x-ray magnetic circular dichroism (XMCD) [4, 5]. By using these techniques it is possible to measure the magnetic properties of supported nanostructures with almost atomic resolution.

Supported Fe clusters have also been the subject of a number of studies, both experimental and theoretical. Among the theoretical ones, Fe has been studied on Cu surfaces, both as mono-atomic wires [6, 7] and as small clusters [8, 9], where enhanced spin and orbital moments have been found. Studies of Fe clusters on Al [10] have found a transition from paramagnetic behaviour for small clusters, to ferromagnetic behaviour for clusters larger than ten atoms. For the subject of this work, Fe on Ni(001), two previous theoretical studies have been reported [9, 11]. These two studies are consistent with each other and the findings are that the spin moment is enhanced for the Fe atoms, compared to what is found for bcc Fe, and that the magnitude of the spin moment is correlated to the number of Fe neighbours in the cluster. In one of these studies [11], the equilibrium structures of the Fe clusters were calculated by means of a modified embedded atom model.

Deposited Fe clusters have been studied experimentally on graphite [4], where the clusters had an average size range of several hundred atoms, and on Ni(001) [5] where the cluster sizes were very small and controlled. For the latter study a strong nonmonotonous variation was found for both the spin and the orbital moments as a function of cluster size. It was proposed that this behaviour might be related to geometric differences between clusters with odd and even numbers of atoms. However, the trend of a strongly varying spin moment was not obtained in subsequent theoretical studies [9, 11], even though several different cluster geometries were considered [9] and the most stable lowest-energy structures were predicted [11].

Despite an exhaustive treatment of the spin moments for Fe cluster on Ni(001) in the previous theoretical studies, no study of the behaviour of the orbital moment for these systems has been reported. In order to address the experimental studies of orbital (and spin) magnetism in these systems, we have calculated both spin and orbital

moments for a selection of small Fe clusters deposited on a Ni(001) surface.

2. Computational Details

The calculations were performed with the RS-LMTO-ASA method [12, 13, 14], which is based on the regular LMTO-ASA technique [16] and uses the Haydock recursion method [17] to calculate the electronic structure by means of the local density of states (LDOS) of the ingoing atoms instead of solving the eigenvalue directly. By employing the recursion method, an $O(N)$ scaling of the computational effort with respect to the system size is obtained. The RS-LMTO-ASA is a fully parameter-free, first-principles method where the spin densities are treated within the local spin density approximation (LSDA) [18].

The electronic structure of the Fe clusters have been performed by embedding them as a perturbation on a previously self-consistently converged 'clean' Ni(001) surface. The charge and magnetisation densities for the cluster atoms and neighbouring Ni atoms are then recalculated self-consistently while the densities for Ni atoms far from the cluster are kept fixed to their values for the unperturbed surface. In order to provide a basis for the wave-function in the vacuum and to treat charge transfers correctly, two layers of empty spheres above the Ni surface are included in the calculations. The procedure for the empty spheres is the same as for the Ni atoms i.e. empty spheres close to the cluster are calculated self-consistently. In all the calculations the LSDA equilibrium lattice parameter for Ni, 3.48 Å, was used.

The Ni surface was modelled by a large cluster of >7000 atoms and the continued fraction, that occurs in the recursion method, has been terminated with the Beer-Pettifor [19] terminator after 30 recursion levels. Both the number of atoms for modelling the semi-infinite surface and the number of recursion steps were tested for convergence.

In order to calculate the orbital moments we perform fully-relativistic calculations where the spin-orbit interaction is treated at each variational step [15]. Details can be found in Ref. [14]. For all cluster sizes, calculations were performed both with and without including the orbital polarisation term (OP) [20]. Furthermore, in the analysis of XMCD spectra one often uses the number of d-holes, which we have calculated as $10-n_d$, where n_d is the d-occupation.

The geometries of the clusters which we have considered can be seen in figure 1. Some of these structures correspond to the most stable solutions obtained by Martínez *et al* [11]. For this particular cases, marked with an asterisk, we have performed calculations with and without including the relaxations found in [11]. The size of the clusters range from two to nine atoms. In some cases we have considered several isomers to explore the influence of the structure in the magnetic properties. In the following text, the different clusters will be referred to according to the labels given in figure 1.

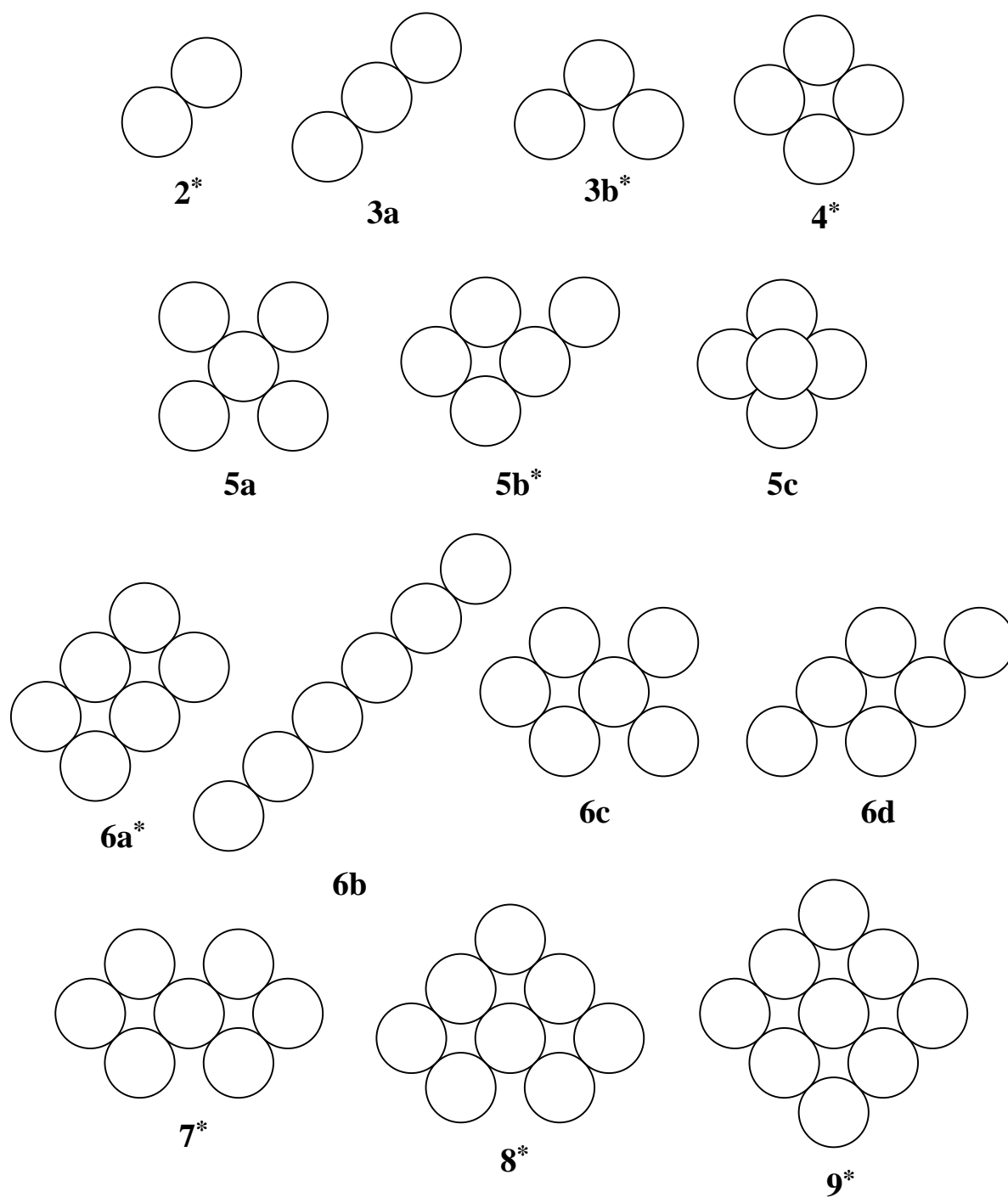


Figure 1. Top view of the structures of Fe clusters on Ni(001) which were used in the calculations. The geometries marked with an asterisk are taken from Martinez *et al* [11].

Table 1. Calculated average spin (μ_s) and orbital (μ_o) moments (in μ_B) and average number of d holes (n_h) for the clusters are shown in figure 1. The two different rows of orbital moments correspond to calculations with orbital polarisation (OP) and without (no OP). On the left results for unrelaxed geometries are shown, whereas on the right we present results for the relaxed geometries taken from [11].

	unrelaxed				relaxed			
	μ_s	μ_o (OP)	μ_o (no OP)	n_h	μ_s	μ_o (OP)	μ_o (no OP)	n_h
2	3.13	0.19	0.10	3.61	3.14	0.21	0.10	3.61
3a	3.11	0.19	0.10	3.60				
3b	3.07	0.16	0.09	3.59	3.08	0.19	0.10	3.57
4	2.95	0.12	0.07	3.53	2.98	0.14	0.08	3.52
5a	3.06	0.15	0.08	3.60				
5b	2.97	0.13	0.08	3.55	2.99	0.15	0.08	3.54
5c	2.83	0.17	0.08	3.49				
6a	2.93	0.12	0.07	3.53	2.94	0.11	0.07	3.55
6b	3.07	0.18	0.09	3.58				
6c	2.98	0.13	0.08	3.56				
6d	2.99	0.14	0.08	3.55				
7	2.93	0.12	0.07	3.53	2.97	0.14	0.08	3.53
8	2.91	0.12	0.07	3.52	2.95	0.13	0.08	3.52
9	2.90	0.12	0.07	3.52	2.94	0.13	0.07	3.52

3. Results

The average spin and orbital moments of the Fe clusters shown in figure 1 are given in table 1, as well as the average number of d holes. We present the orbital moments with orbital polarisation (denoted OP in table 1) and without (denoted no OP). The size of the spin moments and the number of d holes are insensitive to whether orbital polarisation was included or not. We notice that, in general, a decrease of the spin and orbital moments with increasing cluster sizes, even though the change is small. Our calculated spin moments compare well to those reported earlier [9, 11]. Regarding the orbital moments, we find that including the orbital polarisation term results in roughly a doubling of the orbital moment compared to when OP is neglected. The decrease of the average spin and orbital moments with increasing cluster sizes is expected since, in general, larger clusters have higher average coordinations which, as was mentioned in the Introduction, lead to smaller magnetic moments. For those isomers showing a very different average coordination, like 6b, the magnetic moments are also very different. If the number of d holes is considered a similar behaviour is found. There is a decrease of the number of d holes for increasing cluster size, and this variation can be related to the different average coordination. In this case the changes are less important than the ones found for the magnetic moments.

The same trends are valid for unrelaxed and relaxed geometries. In the latter case an increase is observed in general for both spin and orbital moments when compared to

the unrelaxed situation for the same geometry. For spin moments the increase is $0.04\mu_B$ at most, while for orbital moments the maximum increase is $0.03\mu_B$. In all cases the main effect of the relaxation is an expansion of the cluster-substrate distances of around 4%. The expansion decreases the hybridization with the substrate and, therefore, the tendency to magnetism is increased.

The XMCD study reported in [5] found a strong nonmonotonous variation of both spin and orbital moments as a function of cluster size. A comparison between the experimental values and those obtained in this work is found in figure 2, where we show both the calculated spin and orbital moments per d -hole as well as the experimentally found ones. For the sake of clarity, only values corresponding to relaxed geometries are displayed. Starting with the spin moments that are shown in the upper part of figure 2, we see that the majority of our calculated moments are within the reported error bars of the experimental values. Nevertheless, the calculated values are slightly underestimating the spin moments from the XMCD measurements. However, the experimental values for the spin moments include a contribution by the spin magnetic dipolar term $\langle T_z \rangle$, which could be significant for some of the clusters, clearly for those where $\mu_s/n_h > 1$. The inclusion of this term could partly explain the disagreement with the experimental results.

In the lower panel of figure 2, we show the calculated orbital moments as a function of cluster size. The discrepancy between theory and experiment is much larger for the orbital moments than for the spin moments. The smallest calculated orbital moment is found for large clusters, and it has a magnitude of $0.02\mu_B$ per d -hole, while the smallest experimental value is $0.06\mu_B$ per d -hole and it is found for a three-atom cluster. The difference is even more important when larger values are compared: no calculated orbital moment is larger than $0.05\mu_B$ per d -hole, while the largest measured orbital moment is as large as $0.24\mu_B$ per d -hole. It can be noted that, even though the orbital moments are around twice as big when OP was included, the orbital moments are still underestimated in this case. The use of orbital polarisation has in certain cases led to a significant overestimation of orbital moments, but the present results show too small amounts.

In figure 3, the ratio of orbital to spin magnetic moments for the Fe clusters is shown. Given the differences between calculated and measured orbital moments, it is not unexpected that the calculated ratios differ significantly from the measured ones. The largest ratio for the calculated moments is 0.07 with OP, and 0.03 without, while measured ratios range between 0.07 and 0.27. A non-monotonic behaviour is found for the calculated ratio, but it does not seem to have any connection to the behaviour found in the XMCD measurements.

In order to explore the influence of relaxation, the results for relaxed and unrelaxed geometries can be compared in figure 3. As expected from table 1, the ratios are only slightly increased by including the relaxation, and the qualitative disagreement with the experiment is not solved by its consideration, as shown in figure 2.

We have considered several possibilities which could explain the discrepancies with the experimental results. In the light of the calculations, the influence of the geometry

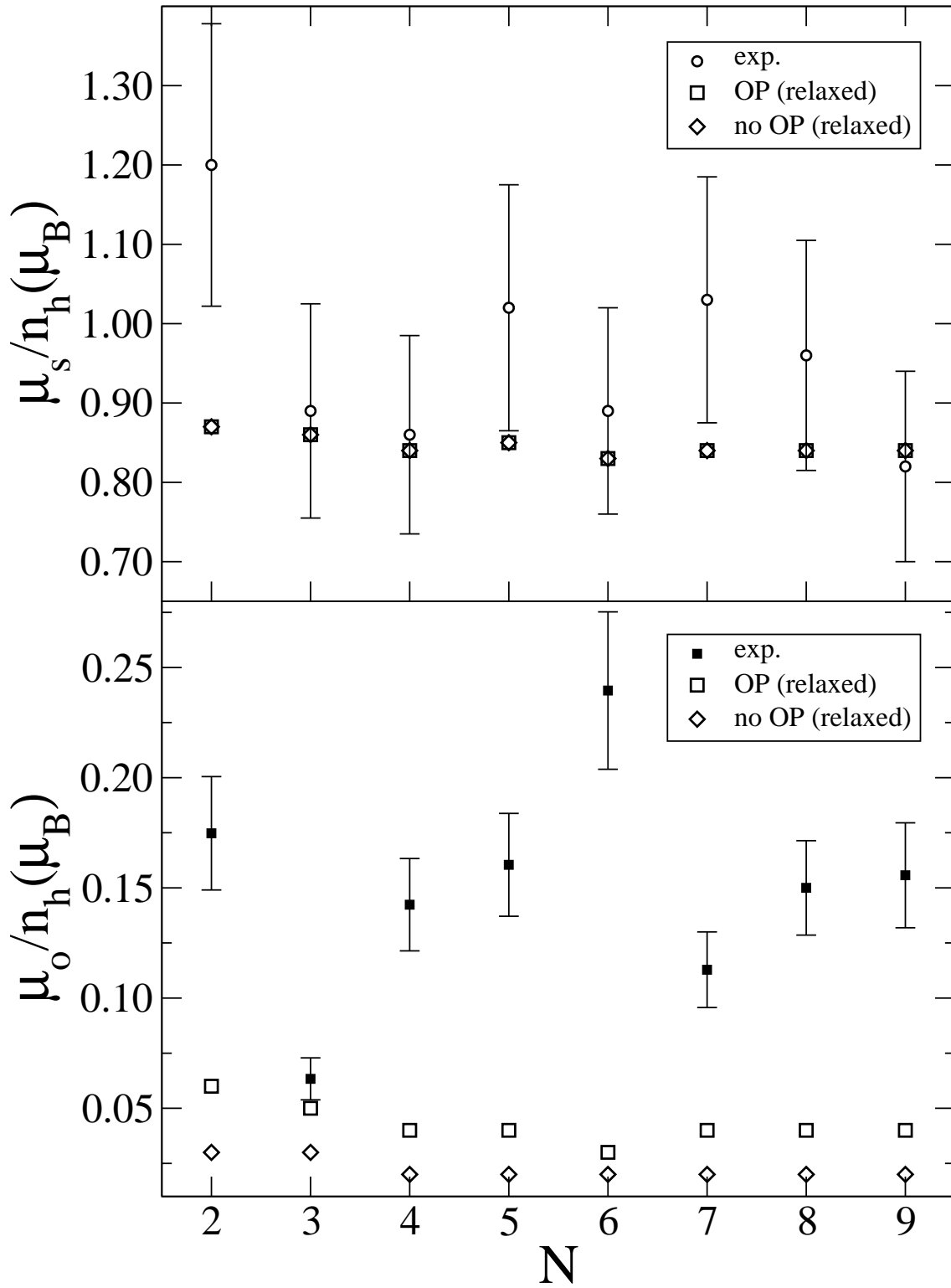


Figure 2. Spin (upper panel) and orbital (lower panel) moments *per d hole* of Ni(001)-supported Fe clusters vs cluster size. The experimental values from [5] are also included.

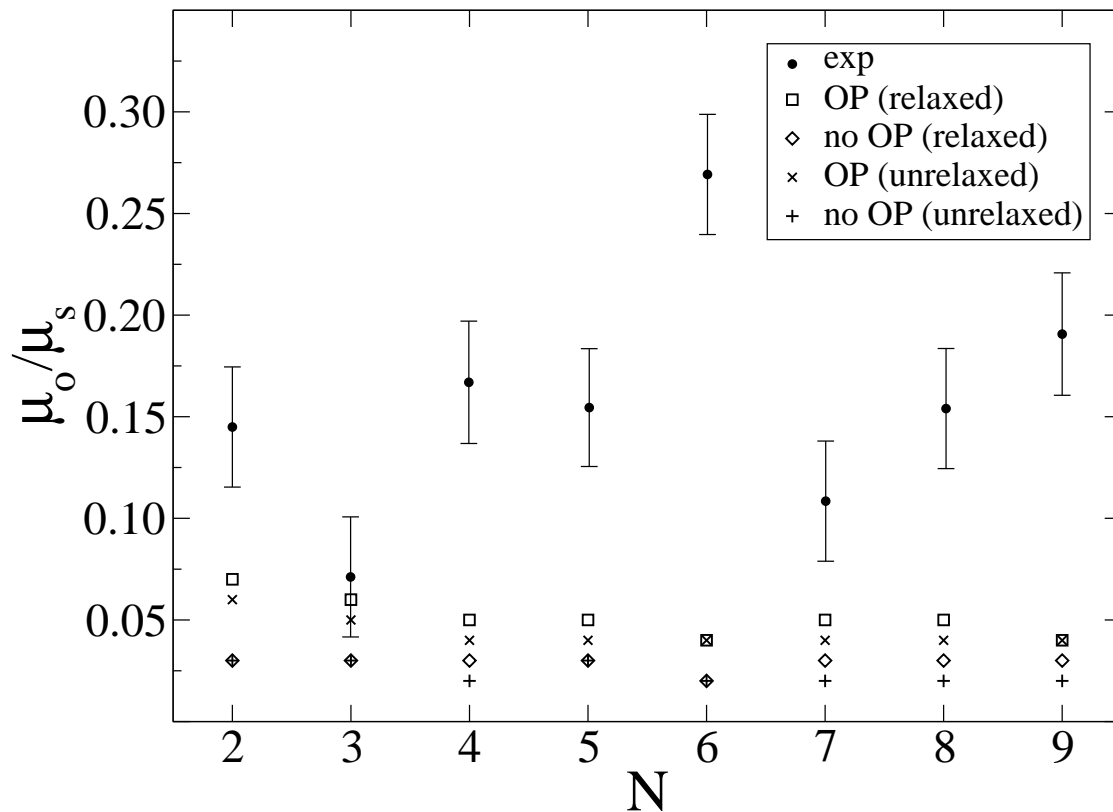


Figure 3. Ratio of Fe_n orbital to spin magnetic moments as a function of cluster size. Unrelaxed and relaxed results are included for those geometries marked with an asterisk in figure 1. The experimental values from [5] are included for comparison.

can be discarded. Particular shapes with small coordination, like linear chains (3a or 6b), lead to an increase of the values for the magnetic moments, but they do not reach the values of the experiment by far. Another possibility is a possible surface intermixing. We have checked this situation by performing calculations for clusters where Fe atoms were replaced by Ni ones. Also in this case, the obtained results can be explained in terms of local coordination. The clusters could also be embedded in the top layer of the Ni cluster. Although experimentally it is an unlikely situation due to the deposition procedure, we have also checked this scenario. As expected, the orbital and spin magnetic moments are smaller in this case than for the supported clusters, due to the increase in the average coordination. In conclusion, none of our calculations was able to shed more light on the mechanism behind the experimental behaviour for the orbital magnetic moments. Instead we conclude that effects beyond those incorporated in LSDA must be responsible for the deviation between measured and calculated orbital moments.

4. Summary and Discussion

We have calculated spin and orbital moments of small Fe clusters supported on a Ni(001) surface. Our obtained spin moments are in good agreement with previous theoretical studies, and they generally agree with the Lau *et al.* experimental ones to within the experimental error. As far as we know, the orbital moments have been calculated here for the first time in these systems. We have found that the orbital moments have an average value between 0.11 and $0.21\mu_B$ when including the OP term, and between 0.07 and 0.10 without including it. These values are much lower than the ones found experimentally. We have also found that the orbital moments non-monotonically decrease as increasing the cluster size, but this behaviour was not related to the much stronger experimental one. Several additional calculations have been performed trying to explain this discrepancy, considering surface intermixing, different cluster shapes or embedded clusters. Neither of these options have been able to explain the experimental behaviour. It is possible that the reason for the discrepancy between experiment and theory lies in that the width of the d-level for these clusters is reduced significantly compared to the corresponding value of bulk of surface geometries. In this way the width of the d-resonance could approach the value of electron-electron interaction (Hubbard U), and the applicability of the local density approximation (or generalised gradient approximation) starts to break down. A possible solution to this problem is to use e.g. the Hubbard-I approximation in combination with first principles theory [21].

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