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Magnetic interactions between small Ni clusters

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Abstract

We have calculated the magnetic moment per atom, $\bar{\mu}$, of symmetric nickel cluster-dimers Ni_N–Ni_N as a function of cluster–cluster distance D and cluster size N. The spin-polarized electronic structure has been calculated with a self-consistent tight-binding method considering the 3d, 4s and 4p valence electrons. We have analyzed the partial sp and d contributions to $\bar{\mu}$. The d component shows a monotonic behavior and provides the dominant contribution to $\bar{\mu}$, whereas the sp contribution shows a non-monotonic (and complex) behavior as a function of the distance and of cluster size. The approaching clusters change their intrinsic magnetic moments at separations of the order of the bulk first nearest-neighbor distance d_{fn}. For $N = 5–7$ there is a range of separations ($1d_{fn}–3d_{fn}$) where the cluster moments are slightly enhanced. © 2000 Published by Elsevier Science Ltd.

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1. Introduction

Since the early 1980s the electronic and structural properties of small atomic clusters have been studied with a main goal in mind: understanding the evolution of these properties from systems with few atoms towards the bulk. In particular a large amount of experimental and theoretical work has been devoted to this important problem in the case of magnetic phenomena [1–12]. The novel magnetic properties present in small magnetic clusters (particularly the large magnetic moments reported) are nowadays considered of fundamental importance for the design of highly advanced electronic components (for a review about this subject, the reader may consult Ref. [13]). The possibility of developing micro-magnetic devices and high-density recording memories by assembling transition-metal clusters appears to be one of the most promising applications. For this reason, a lot of experimental and theoretical attention has focussed on the different nanostructures based on the 3d and 4d elements, like thin films [14–16], super-lattices [17,18] and small clusters (free [1–12] and supported [19–21]). For constructing high-density recording devices, one would like to assemble a two-dimensional array of nearly monodispersed magnetic clusters. The recording density can be enhanced by lowering the cluster size and optimizing their packing, but this packing has a limit because, if the clusters are too close together, the intrinsic properties arising from the small cluster size can be lost. In some natural alloys, the identity of small clusters is maintained by the effect of some buffer atoms that act as a shield preventing the clusters from collapsing into larger entities [22]. The same effect has been applied in self-assembled artificial devices where large metallic clusters are covered by a shield of organic molecules [23]. Thus, knowing the characteristic length determining the interaction between clusters is of extreme importance for constructing efficient cluster assemblies.

As a first step in understanding the assembling of transition-metal clusters to build nanostructures that present novel properties, we study in this paper the magnetic interactions between small Ni clusters. Clusters of sized Ni_3 to Ni_7 with the following structures have been selected: Ni_3 — equilateral triangle, Ni_4 — tetrahedron, Ni_5 — trigonal bipyramid (hexahedron), Ni_6 — octahedron and Ni_7 — pentagonal bipyramid (decahedron). The reason for selecting these geometries is that they correspond to the ground-state structures [8,9] obtained in molecular dynamics simulations using a many-body potential based on tight-binding theory [24]. The selected geometries also

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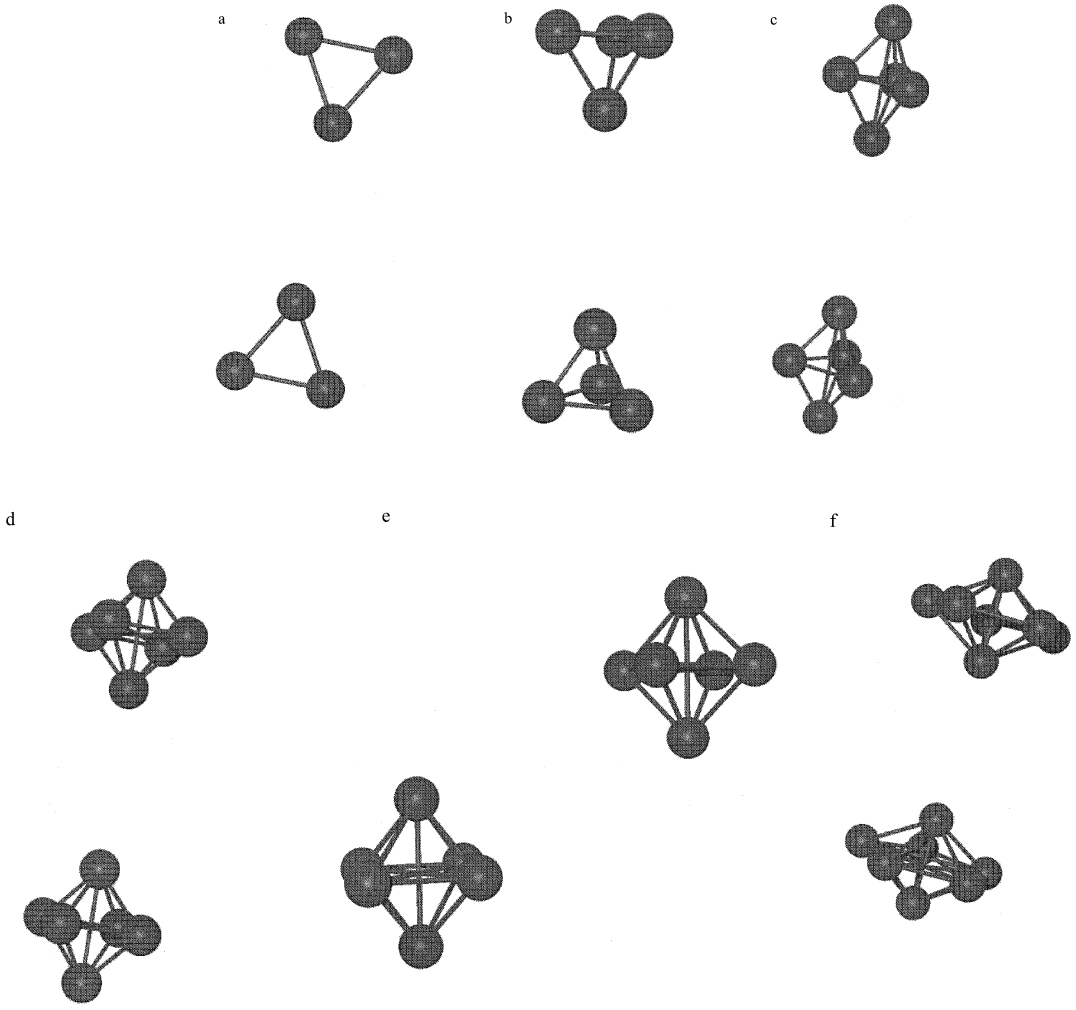

Fig. 1. Snapshots of the process of approach for: (a) Ni_3–Ni_3, (b) Ni_4–Ni_4, (c) Ni_5–Ni_5, (d) Ni_6–Ni_6, and (f) Ni_7–Ni_7. The approaching front is a vertex atom. A second relative orientation is given for Ni_6–Ni_6 (e), with a face as the approaching front.

agree with those obtained in density functional calculations [25,26]. Then, dimers of identical clusters are built, i.e. Ni_3–Ni_3, Ni_4–Ni_4,…, and their electronic structure and magnetic properties are studied as a function of the distance D of approach between the two clusters. The relative orientation of the two clusters is such that the main symmetry axis of each individual cluster coincides with the line of approach, which is also the main symmetry axis of the cluster-dimer and there is mirror symmetry with respect to a plane through the center of mass of the whole system and perpendicular to the line of approach. The distance D is the separation between the two closest atoms, one of each cluster, that lie along the line of approach. A snapshot of the process of approach is shown in Fig. 1 for the five cluster-dimers. The figure also contains a second way of approaching Ni_6–Ni_6 that will be discussed later.

We focus on the study of the average magnetic moment per atom of the cluster-dimers as a function of their distance D. For simplicity, we have also assumed that the structure and inter-atomic distances in the two approaching clusters remain as in the isolated ones, and the process of approach is finished when D becomes equal to the bulk first nearest-neighbor distance (d_{fn}). Our model calculations neglect the role of the substrate in modifying the atomic geometry and electronic structure of the clusters, or in mediating and indirect magnetic interaction between the clusters. The first assumption, concerning the geometry, is justified when the substrate is at low temperature. With respect to cluster–substrate electronic interactions and cluster–cluster interactions mediated by the substrate, these can be important if the substrate is a metal, but are less important for many

insulators, so our calculations are only representative of the second case.

The paper is organized as follows: Section 2 contains the theoretical model used for investigating the electronic structure, the results and their analysis are given in Section 3, and we conclude with a brief summary in Section 4.

2. Model and approximations

The spin-polarized electronic structure has been determined for each geometrical arrangement of the Ni_N–Ni_N cluster-dimers by solving self-consistently a tight-binding Hamiltonian for the 3d, 4s and 4p valence electrons in a mean-field approximation. The non-diagonal elements of the Hamiltonian are assumed spin-independent and are obtained using the Slater–Koster approximation taking the two-center hopping integrals from Papaconstantopoulos [27]. The ratio between the first and second-neighbor hopping integrals fitted by Papaconstantopoulos deviates from the $(r_0/r_{ij})^{l+l'+1}$ law for some Slater–Koster integrals. Nevertheless, tests have been performed that indicated that reasonable changes in the scaling law or in the basic fitted parameters do not produce significant changes in the magnetic moments [28,29]. Since the distance between the two front atoms varies continuously between d_{sn} (second nearest-neighbors) and d_{fn} (first nearest-neighbors) as the clusters approach each other, there is a discontinuity in the variation of the corresponding hopping integrals obtained by the power law prescription at some distance between d_{fn} and d_{sn}. We have verified that the discontinuity is small and does not affect the results.

The diagonal terms of the Hamiltonian are spin-dependent via the electron–electron interaction, which appears as a correction shift of the orbital energy levels in a mean-field approximation

$$\epsilon_{i\alpha\sigma} = \epsilon^0_{i\alpha} + z_\sigma \sum_\beta \frac{J_{\alpha\beta}}{2} \mu_{i\beta} + \Omega_{i\alpha} \qquad (1)$$

where i indicates the atomic site, α and β stand for the type of orbital (s, p, d) and σ is the spin projection. The $\epsilon^0_{i\alpha}$ are bare orbital energies taken from the fit of Papaconstantopoulos [27] for paramagnetic bulk Ni, and consequently do not incorporate the magnetic contribution, although they implicitly include the rest of the electron–electron interactions as well as the effect of the crystalline field of the bulk. The changes of the last two contributions, when one considers the clusters instead of the bulk, are accounted for by the potentials $\Omega_{i\alpha}$. The second term in Eq. (1) is the spin-dependent shift due to the spin-polarization $\mu_{i\beta} = n_{i\beta\uparrow} - n_{i\beta\downarrow}$ of the electrons, calculated from the occupation numbers $n_{i\beta\sigma}$. In this term, $J_{\alpha\beta}$ represents the exchange interaction parameters and z_σ is the sign function ($z\uparrow = 1, z\downarrow = -1$). All the exchange parameters involving s and p electrons are neglected and J_{dd} is fitted in order to reproduce the bulk magnetic moment, with the result $J_{dd} = 1.2336$ eV. Note that spin-polarization of the de-localized sp-band also occurs as a consequence of the hybridization with the spin-polarized d-states. Finally, the site- and orbital-dependent potentials $\Omega_{i\alpha}$ are self-consistently determined so as to assure the sp and d electronic occupations at each atomic site in the cluster — fixed in our model by a linear interpolation between the isolated atom (d^8, s^2, p^0) and the bulk ($d^{9.1}$, $sp^{0.9}$) electronic configurations according to the local coordination number — and assuming local charge neutrality, that is a total of 10 spd electrons at each site. We have considered different potentials for the localized d-states (Ω_{id}) and for the de-localized sp-states ($\Omega_{is} = \Omega_{ip}$).

The spin-dependent local electronic occupations are self-consistently obtained by integrating up to the Fermi level the local densities of states, which are calculated at each iteration by using the recursion method [30]. This tight-binding formalism has been applied [8] to calculate the magnetic moments of gas-phase Ni_N clusters and, in the range of small cluster sizes, the formalism accurately reproduces the variation of the magnetic moment with N measured by Apsel et al. [3]. Often several metastable self-consistent solutions are obtained for the magnetic moments in small clusters of transition elements. In the case of isolated Ni_N clusters, previous experience indicates that the coupling between the magnetic moments at the different atomic sites is ferromagnetic [31], but nothing is known about the coupling between the magnetic moments of neighbor clusters, which is the case of interest here. For this reason, we have investigated different magnetic couplings and found that coupling between Ni clusters is also ferromagnetic.

3. Results

The first issue in the calculation is to choose an adequate cutoff for the long-range electronic interactions. For interatomic distances larger than this cutoff, the corresponding hopping integrals are zero. This reduces the number of interaction terms and, therefore, the computational effort. It is clear that the cutoff has to be large enough to take into account the cluster–cluster interactions when these are not too far apart. The largest distance within the atoms in the individual clusters considered here is $r_1 = 1.58$, taking the first nearest-neighbor bulk distance (d_{fn}) as unity, and occurs in the decahedral cluster (pentagonal bipyramid), so a cutoff equal to $2r_1 = 3.16$ seems a reasonable choice.

The calculated average magnetic moments for the cluster-dimers as a function of dimer separation D are given in Fig. 2. The dependence on D is complex, so it is convenient to analyze first the d and sp components of μ separately. In Fig. 3 we show the d contribution of the average magnetic moment as a function of separation D. The behavior is similar for all cluster-dimers. By decreasing the separation between clusters, the interactions grow and the d-magnetic moment decreases monotonically. There is a sharp drop near $D = 1$ for Ni_4–Ni_4 and also occurs for Ni_3–Ni_3, but is not

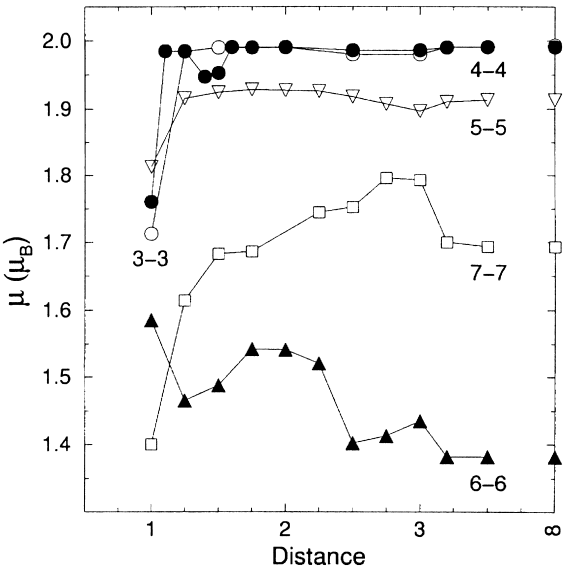

Fig. 2. Average magnetic moment as a function of the separation between clusters. The limit of infinite separation is indicated on the right side.

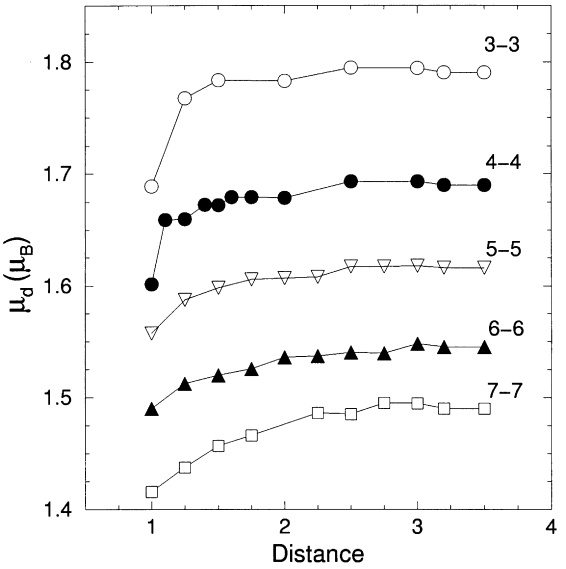

Fig. 3. Behavior of the d contribution to the average magnetic moment as a function of the distance D between the two clusters.

noticeable for N larger than 4 because, with increasing N, the relative contribution of the front atoms is attenuated. Comparing the different curves in this figure, we observe that μ_d also decreases monotonically with N. All these results can be rationalized by the known rule that the magnetic d-moment decreases with the increasing average coordination. An increase in the average coordination produces a widening of the d-band that leads to a lowering of the density of states all over the d-band and, in particular, at the Fermi level (this is especially evident in the simple square-band model of Friedel [32]) and, in this way, the d-magnetic moment also decreases. The increase in the local coordination, especially of the front atoms, occurs by approaching the two clusters. On the other hand, by increasing N, the average coordination also increases. Therefore, the d-magnetic moment decreases from the top to the bottom curves in Fig. 3.

The sp contribution shows a more complex behavior as we show in Fig. 4. In the upper panel we see the cluster-dimers for $N = 3$ to 5 and in the lower panel for $N = 6, 7$. The behavior of μ_{sp} depends sensitively on N. It is worth noticing that in the cluster-dimers based on clusters with an odd symmetry axis ($N = 3, 4, 5, 7$), the sp contribution to the magnetic moment points, in general, in the same direction as the d contribution (except in Ni_7–Ni_7 for $D = 1$). Instead, μ_{sp} shows a marked oscillating behavior around a zero value for the cluster with an even-symmetry axis (octahedral cluster) and for some cluster–cluster separations μ_{sp} and μ_d point in opposite directions. As expected, the d contribution to $\bar{\mu}$ is dominant in all cases (80–90%), although the sp contribution is by no means negligible and has to be included necessarily in the calculations in order to obtain quantitative values of $\bar{\mu}$, especially since its effect can be either enhancing or lowering $\bar{\mu}$, depending on the geometry of the clusters.

We now return to discuss the average magnetic moments $\bar{\mu}$ of Fig. 2. We can see that its complex dependence on D and N is led by the sp contribution. For large distances, the two clusters *do not see* each other and the value of the magnetic moment is one of the isolated clusters. As we bring the clusters together, they *feel* each other when the atoms of the second cluster come into the interaction range of the atoms of the first cluster (determined by the cutoff). A related effect is that by reducing the distance between the two clusters, the average coordination increases and this reduces the value of the d-magnetic moment. The triangular, tetrahedral, hexahedral and decahedral clusters behave roughly in the expected way in terms of D. Nowadays, we know that the electronic structure of the small systems is the result of a balance between inter-related electronic and geometrical factors, which account for the singular behavior of the octahedral dimer. A characteristic feature for $N = 5, 6, 7$ is that the average magnetic moments for some cluster separations are larger than the average magnetic moment for infinite separation (that is, for the non-interacting clusters). This is not too surprising, considering the fact that the measured average magnetic moment of nickel clusters [1–3] is not a simple monotonous function of cluster size; instead, it displays pronounced oscillations, arising mainly from the geometrical details associated to cluster growth. It is well known nowadays that an enhancement of the magnetic moments is one of the main goals to be achieved in building nanostructures.

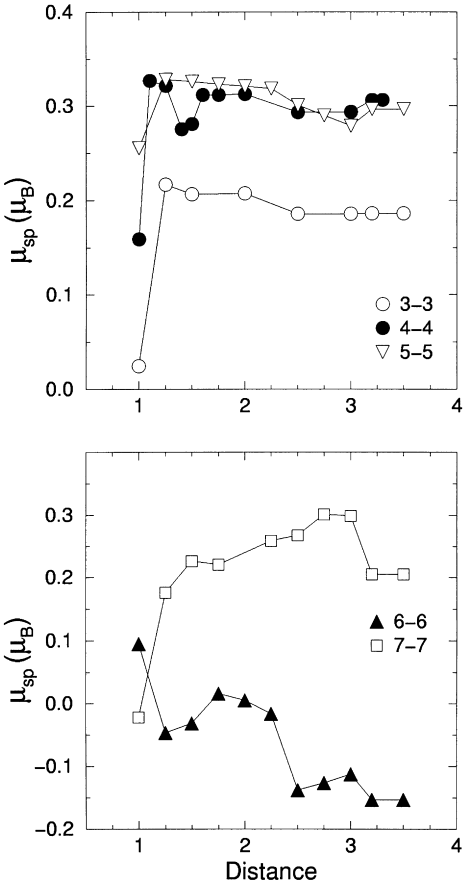

Fig. 4. Behavior of the sp contribution to the average magnetic moment as a function of the cluster–cluster distance D.

A relevant question concerns the critical inter-cluster separation D_c, below which the two clusters forming the dimer lose their intrinsic properties, in this case the intrinsic magnetic moment. For very small cluster, $N = 3$–5, this critical distance seems to be close to the nearest-neighbor distance in the bulk, which is $D = 1$ in our units. For larger clusters, $N = 6, 7$, D_2 is larger and the magnetic properties of the two approaching clusters seem to be affected already at separations $D = 2.5$–3.

In Fig. 5 we analyze the effect of the relative orientation, so that the approaching front is formed by two anti-oriented triangular faces (see Fig. 1). The cluster separation in this case is the distance between the centers of those two faces. The results for the magnetic moment of this case (Oct-II) are compared with the previous cluster-orientation (Oct-I). μ_d has a similar rather monotonous behavior in both cases (see Fig. 5b). However, the values for Oct-II are slightly smaller, as expected from the larger value for the average coordination produced by a face front as compared to a vertex front. The μ_{sp} is very sensitive to the relative cluster-orientation, especially for separations $D > 2$ (Fig. 5a). Consequently, the oscillation of the total magnetic moment with D is

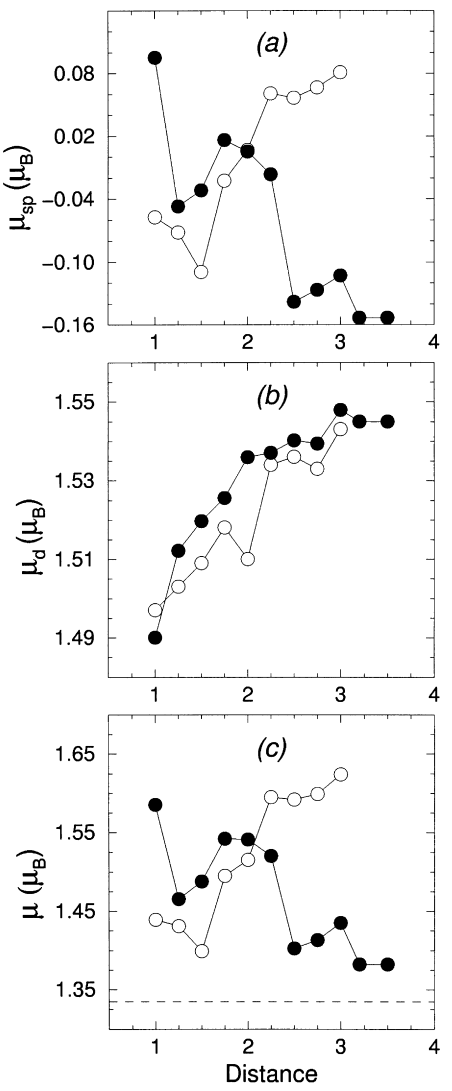

Fig. 5. The effect of the relative orientation of the approaching clusters. sp (panel (a)) and d (panel (b)) contributions to the average magnetic moment (panel (c)) as a function of cluster–cluster distance D, for octahedral cluster-dimers. The symbol (●) corresponds to Oct-I and (o) to Oct-II, as discussed in the text.

different for Oct-II and Oct-I, and Oct-II behaves more in the expected way, in contrast to Oct-I. The dotted line in Fig. 5c indicates the value of the magnetic moment per atom for Ni_{12} in its icosahedral ground-state geometry. The Ni_6–Ni_6 dimer is much less compact than Ni_{12} and this accounts for the larger magnetic moments of the cluster-dimer at all cluster separations and, in particular, around $D = 1$.

4. Summary and comments

We have calculated the average magnetic moment for

unsupported Ni_N–Ni_N cluster-dimers as a function of cluster–cluster distance for different cluster sizes (N = 3–7). The d component of the magnetic moment provides the dominant contribution and shows a monotonous behavior with cluster–cluster separation and with varying cluster size. The sp component shows instead a complex behavior with a strong dependence on the size of the clusters. This complex behavior reflects itself in the total magnetic moment, leading to the general conclusion that the sp electrons have a marked influence on the electronic properties of small nickel clusters, as was shown in previous works [8,9]. Two different relative orientations of approach were studied for Ni_6–Ni_6 and it is concluded that this variable also has a marked influence on the magnetic moments. With a view on the possible applications in magnetic nanodevices, we conclude that the individual clusters do not lose their intrinsic magnetic moment until they are at rather short separations, on the order of the nearest-neighbor bulk inter-atomic distances. Even more, we find in some cases an enhancement of the moments for cluster–cluster separations a little larger (twice or three times) than the bulk inter-atomic distances. This enhancement is in all cases small.

In this work we have assumed that the clusters retain their geometrical structure during the process of mutual approach. This is a valid assumption because we are interested in the collapsing of the clusters; instead our aim has been to investigate the behavior of the magnetic properties under conditions where the clusters do not collapse. Another assumption is that the fixing of the inter-atomic distances inside a cluster can be easily relaxed, although it is not expected to induce qualitative changes in our results and conclusions.

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