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Magneto-structural properties and magnetic anisotropy of small transition-metal clusters: a first-principles study

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Abstract

Ab initio density-functional calculations including spin–orbit coupling (SOC) have been performed for Ni and Pd clusters with three to six atoms and for 13-atom clusters of Ni, Pd, and Pt, extending earlier calculations for Pt clusters with up to six atoms (2011 J. Chem. Phys. 134 034107). The geometric and magnetic structures have been optimized for different orientations of the magnetization with respect to the crystallographic axes of the cluster. The magnetic anisotropy energies (MAE) and the anisotropies of spin and orbital moments have been determined. Particular attention has been paid to the correlation between the geometric and magnetic structures. The magnetic point group symmetry of the clusters varies with the direction of the magnetization. Even for a 3d metal such as Ni, the change in the magnetic symmetry leads to small geometric distortions of the cluster structure, which are even more pronounced for the 4d metal Pd. For a 5d metal the SOC is strong enough to change the energetic ordering of the structural isomers. SOC leads to a mixing of the spin states corresponding to the low-energy spin isomers identified in the scalar-relativistic calculations. Spin moments are isotropic only for Ni clusters, but anisotropic for Pd and Pt clusters, orbital moments are anisotropic for the clusters of all three elements. The magnetic anisotropy energies have been calculated. The comparison between MAE and orbital anisotropy invalidates a perturbation analysis of magnetic anisotropy for these small clusters.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In modern magnetic recording technologies, bits of information are stored in magnetically stable domains and a large magnetic anisotropy energy, determining the barrier to magnetization reversal due to thermal excitations, is therefore required to inhibit loss of information [1, 2]. A high magnetic anisotropy energy requires large spin and orbital moments and a strong spin–orbit coupling. Furthermore, a reduction of the size of the domain carrying one bit of information necessitates an increase of the magnetic anisotropy energy per atom. In nanostructures (ultrathin films, chains and clusters) the magnetic spin and orbital moments are enhanced over their bulk values because of the reduced dimensionality and reduced coordination number, and this is expected to lead to a strongly enhanced MAE. Therefore, the novel magnetic properties of nanostructures have received increasing attention during the past decade [3–6]. The ultimate limit of miniaturization is reached for small metallic clusters.

The magnetic properties of small transition-metal clusters have been studied extensively in the past, both experimentally [3–5, 7–11] and theoretically [6, 12–23]. Attention has focused in particular on 13-atom clusters, where generally
the formation of icosahedral structures had been expected. Recent ab initio studies predicted different structures for the 4d and 5d metals, without, however, reaching agreement on the ground-state configurations [14–23]. Stern–Gerlach experiments found strongly enhanced magnetic moments in small Ni clusters, reaching nearly three times the value in ferromagnetic fcc Ni. It has also been demonstrated that small clusters of 4d and 5d metals, such as Rh, Pd, or Pt, which are non-magnetic in the bulk, carry a magnetic moment. Since the spin–orbit coupling in these heavy elements is much stronger than in the magnetic 3d metals, small clusters of these elements are expected to have a large MAE. From the theoretical side, spin-density-functional theory (SDFT) offers an efficient way to study magneto-structural properties of nanostructures. However, to date most theoretical studies have been performed in a non-relativistic or scalar-relativistic mode, providing detailed information on the geometrical properties and on the magnetic spin moments, but not on orbital moments and magnetic anisotropies (see [13–15, 23] and further references given therein). While the calculation of orbital magnetic moments and of the magnetic anisotropy of small metallic clusters in the gas phase has been attempted in a number of studies based on semi-empirical tight-binding schemes [24–28], only a few relativistic ab initio studies have addressed this problem using SDFT [23, 29–38] and quantum-chemical methods [39, 40]. In addition, relativistic studies of magnetic atoms and clusters supported on non-magnetic metallic surfaces of heavy metals using SDFT techniques have been reported [24, 28, 41–47]. In this case the magnetic anisotropy is determined by the interplay between the large magnetic moment of the adatoms and the strong spin–orbit coupling in the substrate.

Huda et al [30] investigated the effect of spin–orbit coupling on the geometric structures of Pt\(_n\) clusters (\(n = 2, \ldots, 5\)) and reported that relativistic effects lead to a preference for planar structures, but did not report any magnetic data. Piotrowski et al [23] examined the effect of spin–orbit coupling on the atomic structure of 13-atom clusters formed by transition-metals and reported only modest changes in the structural energy differences for the transition metals, while for Au\(_{13}\) SOC was found to favor the formation of three-dimensional over planar structures (in contrast to the results for smaller Au clusters). Again no results on orbital moments and magnetic anisotropies were reported. The results of Huda et al have been contested by Sebecti [31], who reported three-dimensional structures also for Pt tetra- and pentamers. Fernández-Seivane and Ferrer [32] performed spin-density-functional calculations of the magnetic anisotropy energies for selected Pd, Pt, Ir and Au clusters with up to seven atoms, but with SOC implemented only in an on-site approximation. Strandberg et al [33], Fritsch et al [35] and Blöński and Hafner [36] investigated the magnetic anisotropy of a series of dimers of late transition metals from the Fe, Co and Ni groups and attempted to relate the MAE to the splitting of the eigenstates caused by spin–orbit coupling and the increasing filling of the d states. Strandberg et al [33] used the SDFT results to construct a giant-spin Hamiltonian that allows the investigation of the angular-dependence of the magnetic anisotropy energies. Later work by Strandberg et al [34] extended the investigations to Co\(_n\) (\(n = 2, \ldots, 5\)), Mn\(_n\)\(_n\), and Co\(_2\)Fe\(_2\) clusters. Sahoo et al [38] reported ab initio investigations of the MAE of 13-atom clusters of Fe, Co, and Ni, concentrating on the influence of symmetry. For clusters with the structure of an ideal icosahedron, MAE’s of 1.7, 0.31, and 0.77 μeV/atom, comparable to the MAE of the bulk metals, have been reported for Fe\(_{13}\), Co\(_{15}\), and Ni\(_{13}\), respectively. In this case, because of the high symmetry of the cluster, the leading contribution to the MAE is sixth order in the SOC. A geometric distortion lowering the symmetry was found to enhance the MAE by orders of magnitude. For Fe\(_{13}\) an MAE of 0.32 meV/atom was reported for a ‘Jahn–Teller-distorted’ cluster. However, only a restricted relaxation of the icosahedral structure describable by one-parameter models was permitted and the optimization was performed in a scalar-relativistic mode, such that the possible influence of the SOC on the cluster structure was not considered. Very recently Blöński et al [37] performed relativistic calculations of the structural and magnetic properties of Pt\(_n\), \(n = 2–6\) clusters. In agreement with Huda et al it was found that for clusters consisting of up to five atoms SOC leads to a preference for planar structures and that even for a six-atom cluster the energetic ordering of different isomers is reversed. SOC leads to the formation of large orbital magnetic moments and to a mixing of different spin states. Due to the spin-mixing the total magnetic moment may be larger or smaller than the spin moment in the absence of SOC. Both spin and orbital moments are found to be anisotropic. Because of the strong SOC the energy differences between coexisting magnetic isomers can be comparable to or even smaller than their magnetic anisotropy energies. In this case the lowest barrier for magnetization reversal can be determined by a magnetic isomer that is different from the ground-state configuration. This result is closely related to the finding of Smogunov et al [48], who showed that for freestanding Pt–monowires ferromagnetic ordering is observed for a magnetization perpendicular to the axis of the wire, while magnetization disappears if the moments are forced to align parallel to the axis. Hence in this case the ‘giant’ MAE is a demagnetization energy.

These results are important for assessing the validity of simplified theories of the MAE. A well known expression for the MAE was derived by Bruno [49] within perturbation theory, assuming that the majority band is completely filled and that the spin moments are isotropic. In this case the MAE is proportional to the spin–orbit coupling parameter \(\xi\) and to the difference in the expectation values of the orbital moment calculated for the easy and hard axes of magnetization, i.e. to the anisotropy of the orbital moment. Bruno’s theory has been extended by van der Laan [50] to account for terms contributing to second order and for a possible weak anisotropy of the spin moment. Similarly, the description of the MAE in terms of an effective Hamiltonian with a single giant-spin degree of freedom given by Strandberg et al [33, 34] assumes that the size of the effective spin moment remains unchanged upon rotation to the magnetization directions. Both descriptions cannot account for the results derived for Pt clusters and monowires.
Pt clusters with their strong SOC are a special case because only the smallest clusters are magnetic. Magnetism has been reported to disappear already for a cluster with about 13 or slightly more atoms. In the present work we have extended the investigations to Ni and Pd clusters. Clusters of the late 3d and 4d metals tend to be quite strongly magnetic [14, 15] and their larger spin moments might at least partly compensate for the weaker SOC.

2. Computational details

The electronic structure calculations and structural optimizations reported here have been performed employing the Vienna ab initio simulation package VASP [51, 55]. VASP performs an iterative solution of the Kohn–Sham equations of density-functional theory within a plane-wave basis and using periodic boundary conditions. A semilocal functional in the generalized gradient approximation (GGA) [52] (PW91) and the spin-interpolation proposed by Vosko et al [53] are used to describe electronic exchange and correlation and spin-polarization. The projector-augmented wave (PAW) method [54, 55] is employed to describe the electron–ion interactions. The PAW approach produces the exact all-electron potentials and charge densities without elaborating nonlinear core-corrections, which is particularly important for magnetic elements.

The PAW potentials have been derived from fully relativistic calculations of the atomic or ionic reference calculations. Spin–orbit coupling has been implemented in VASP by Kresse and Lebacq [56]. Following Kleinman and Bylander [57] and MacDonald et al [58], the relativistic Hamiltonian given in a basis of total angular momentum eigenstates $|j, m_j\rangle$ with $j = l \pm \frac{1}{2}$ (containing all relativistic corrections up to order $\alpha^2$, where $\alpha$ is the fine-structure constant) is recast in the form of $2 \times 2$ matrices in spin-space by re-expressing the eigenstates of the total angular momentum in terms of a tensor product of regular angular momentum eigenstates $|l, m\rangle$ and the eigenstates of the $z$-component of the Pauli-spin matrices. The relativistic effective potential consists of a term diagonal in spin-space which contains the mass velocity and Darwin corrections, and the spin–orbit operator,

$$ V = V^\text{nc} + V^\text{SO} = \sum_{l,m} [V_l \cdot \mathbf{L} + V^\text{SO}_l \mathbf{L} \cdot \mathbf{S}] |l, m\rangle \langle l, m|, $$

where $1_l$ is the unit operator in spin-space and

$$ \mathbf{L} \cdot \mathbf{S} = \frac{1}{2} \begin{pmatrix} L_x & L_z \\ L_z & -L_x \end{pmatrix}. $$

The $l$-components of the scalar $V_l$ and spin–orbit $V^\text{SO}_l$ potentials are weighted averages over the $l \pm \frac{1}{2}$ components, assuming that the magnetization is directed along the $z$-axis. The Hamiltonian is therefore a $2 \times 2$ matrix in spin-space. The nondiagonal elements arise from the spin–orbit coupling, and also from the exchange–correlation potential when the system under consideration displays a noncollinear magnetization density. Calculations including spin–orbit coupling have, therefore, to be performed in the noncollinear mode implemented in VASP by Hobbs et al [59] and Marsman and Hafner [60]. The Kohn–Sham equations with the relativistic effective potential have been solved self-consistently. Forces acting on the atoms have been calculated using the Hellmann–Feynman theorem.

The smallest clusters were placed into a $10 \times 10 \times 10 \AA$ cubic box, being large enough to suppress any interactions between the periodically repeated images of the clusters. The size of the box has been extended to $15 \times 15 \times 15 \AA$ for the larger 13-atom clusters. Geometric, electronic and magnetic degrees of freedom were relaxed simultaneously without any constraint until the change in total energy between successive iteration steps is smaller than $10^{-7}$ eV. The calculations were performed in two steps. First a collinear scalar-relativistic calculation has been performed. The geometry optimization has been performed by a static relaxation using a quasi-Newton method, starting from different initial configurations, including both three-dimensional and planar structures. For clusters with 13 atoms, in addition, molecular-dynamics simulations followed by a dynamical simulated annealing have been performed (details can be found in the paper by Futschek et al [14, 15]). In addition, structures proposed on the basis of other algorithms for searching global energy minima [16, 23] have been examined. In the second step the configurations resulting from the scalar-relativistic calculations were used to initialize the noncollinear calculations, including spin–orbit coupling [59, 60], allowing again for a relaxation of all geometric, electronic and magnetic degrees of freedom. For each structural isomer of a cluster a set of self-consistent calculations with different initial orientations of the magnetic moments was performed to find the easy and hard magnetic axes and to calculate the MAE in terms of the difference in the total energies. For each initial configuration all structural, electronic, and magnetic degrees of freedom have been optimized without any symmetry constraint, but for the converged solution the magnetic point group symmetry has been determined.

The basis set contained plane waves with a maximum kinetic energy of 500 eV, a convergence of the total energy within $10^{-7}$ eV was imposed during the self-consistency cycle. The cluster structure was relaxed without any symmetry constraints until the forces on all atoms were less than 10 meV Å$^{-1}$. We have checked that the results remain unchanged for higher cut-off energies and even more stringent criteria for convergence. Calculations were performed for the $\Gamma$-point of the computational cell only. The total magnetic moments of the clusters are calculated from the difference in the integrated spin-polarized densities of states. This is possible because spin and orbital cluster moments are always collinear. Local spin and orbital moments are determined by projecting the plane-wave components of the eigenstates onto spherical waves inside slightly overlapping atomic spheres. Because this projection depends on the choice of the atomic radius, the sum of the local moments is not necessarily identical to the total cluster moment.

3. Results

Some of the effects of spin–orbit coupling have already been documented in earlier studies [30, 37], and these findings have
been confirmed by our calculations. (i) The SOC energies per atom (defined as the difference in the total energies with and without SOC) show only a modest variation with the size of the cluster. For Pt clusters, the values oscillate around 0.45 eV/atom [30, 37], they are much smaller for Pd (~0.05 eV/atom) and Ni (~0.01 eV/atom) clusters. (ii) The binding energy of the clusters, calculated with respect to the separated-atom limit, is reduced by SOC for Ni (by about 0.035 eV/atom) and Pt (by about 0.20 eV/atom) cluster, because SOC makes a larger contribution to the total energy of the isolated atoms with an open d shell (electronic configuration d^9s^1), see figure 1. For Pd clusters, SOC enhances the binding energies on average by about 0.02 eV/atom because the SOC energy of the free atoms with their closed d^{10} shell does not outweigh the corrections to the total energy of the clusters. For Ni_{12}, the reduction of the binding energies leads to slightly better agreement with the experimental values of Grushow and Evin [69], $E_b = 1.44/1.58/1.70/2.04$ eV/atom for $n = 3–6$, to be compared with $E_b = 1.92(1.89)/2.22(2.18)/2.47(2.43)/2.69 (2.65)$ eV/atom from theory (SOC corrected values in parentheses), although it should be emphasized that experimental binding energies are subject to large uncertainties. No experimental values are available for Pd and Pt clusters. (iii) The influence of SOC on the cluster geometry is modest in most cases. Changes in bond lengths are very small, usually less than 0.01 Å. (iv) For Ni and Pd clusters the energetic order of different structural isomers remains unchanged, while for Pt_{n} clusters SOC favors planar structures for $n$ up to 5 [30, 37]. In the following, the discussion will concentrate on the magneto-structural properties of transition-metal clusters, and the correlation between their geometry and magnetism.

3.1. Trimers

The scalar-relativistic calculations for Ni and Pd trimers predict a ground-state configuration forming an equilateral triangle, a magnetic spin moment of $\mu_S = 2\mu_B$ (i.e. $S = 1$, spin triplet), and bond lengths of 2.20 and 2.52 Å, respectively. For this highly symmetric configuration the highest molecular orbital is triply degenerate, but occupied by only two electrons. Hence it is expected that the cluster undergoes a Jahn–Teller distortion lowering the symmetry from $D_{3h} = 6m2$ to $C_{2v} = mm2$. According to the calculations by Futschek et al [14, 15], for a Ni_{3} trimer a minimal distortion with a difference of 0.01 Å between one short and two long bonds occurs, while for Pd_{3} and Pt_{3} $6m2$ symmetry is preserved. The stability of Pd and Pt trimers at the SDFT level against Jahn–Teller distortion is consistent with other SDFT calculations, while Balasubramaniam et al [39, 61] and Valerio and Toulhoat [62] have shown that calculations at a multiconfiguration Hartree–Fock level or using hybrid functionals mixing Hartree–Fock and DFT exchange predict a broken symmetry. However, it must be pointed out that the deviations from perfect threefold symmetry reported there are very modest, with differences in the bond lengths around 0.01 Å and in the bond angles of the order of 0.02°–0.04°.

The calculations including spin–orbit coupling have been initialized with three different orientations of the magnetization direction: in-plane, along the z-direction (i.e. along a twofold symmetry axis of the equilateral triangle—for the definition of the coordinate system see figure 2), out-of-plane, along the y-direction, and along the [111] direction. For in-plane and out-of-plane orientations the total energy is stationary with respect to a rotation of the magnetic axis. The former represents the easy, the latter the hard magnetic axis. The difference in the total energies defines the MAE, which is 2.35 and 0.85 meV/atom for Ni and Pd trimers, respectively. For an initially oblique direction, the magnetic axis relaxes to the in-plane orientation. For the Ni_{3} cluster in this relaxed state, the moments form an angle of about 30° with the easy axis, i.e. they are oriented along one of the edges of the triangle and the energy difference of 0.1 meV defines the very low in-plane anisotropy energy. For the Pd_{3} trimer the angle with respect to the easy axis is about 60°, i.e. the magnetization relaxes to a symmetry-equivalent easy axis, and the total energy difference is only 0.02 meV/atom—essentially on the edge of the computational accuracy.

The orientation of the magnetic axis can break the symmetry of the cluster. For a magnetization axis perpendicular to the plane of the trimer, the threefold symmetry is conserved. The magnetic point group (MPG) symmetry 6$m'2$’ (in Hermann–Mauguin notation [63], a prime attached to a symmetry operation indicates that this operation must be combined with a time-reversal operation which reverses the direction of axial vectors such as the magnetic moment) is compatible with the ferromagnetic alignment of the local moments along the main symmetry axis. For an in-plane magnetization direction both the geometric and the magnetic symmetry are reduced to orthorhombic. We find isosceles triangles for both trimers, with two short and one long edge for the Ni_{3} and two long and one short edge for the Pd_{3} cluster (see figure 2). However, while the geometric distortions are modest (differences in bond lengths do not exceed 0.02 Å), large differences appear in the local magnetic moments. The MPG is $m'm'2$, compatible with the parallel alignment of the local spin moments and the canting of the local orbital moments towards the twofold symmetry axis. The local total magnetic
moments are larger on the atom occupying the vertex pointing along the easy axis, i.e. oriented along the mirror plane of the structure (see figure 2). Total spin and orbital moments of the cluster and the local spin and orbital moments at the site with the highest moment are always collinear, but on the other two sites spin and orbital moments are canted by angles varying between ±25° (Pd₃), ±46° (Pt₃) and ±48° (Ni₃) and the local spin moments are also slightly canted relative to the global magnetization axis, see figure 2.

While in a scalar-relativistic description both trimers have a spin moment of $2 \mu_B$ ($S = 1$), SOC induces a mixing of different spin states with the largest contributions coming from low-lying spin isomers. For the Ni trimer, both low- and high-spin isomers have high excitation energies (larger than 77 meV) in the scalar-relativistic approximation, while for Pd₃ $S = 1$ and $S = 0$ isomers are energetically degenerate [14, 15]. Consequently, the relativistic calculations yield a spin moment which is slightly enhanced for Ni ($\mu_S = 2.19 \mu_B$), but reduced for Pd ($\mu_S = 1.66 \mu_B$). The orbital moments increase with increasing strength of the SOC as expected, we find $\mu_L = 0.58$, 0.93 and 1.07 $\mu_B$, and $\mu_J = 2.77$, 2.59 and 2.54 $\mu_B$ for Ni, Pd and Pt [37] in their easy-axis orientation, respectively.

Spin and orbital moments of the clusters show different degrees of anisotropy: for Ni₃ the spin moment is isotropic, but the orbital moment is strongly reduced for the out-of-plane
μPt3. The MAE is calculated as the energy difference between calculations using the local-density approximation (LDA) and gradient-corrected functionals (GGA results given in parentheses). The easy-axis orientation described in their paper is also in-plane with noncollinear local spin moments for Pt3. The MAE is calculated as the energy difference between this ground-state configuration and the first excited magnetic isomer with out-of-plane orientation. Information on the cluster geometry and on the spin and orbital magnetic moments can be found in the supplementary information to their paper. Quite generally we find that for most clusters these authors report larger spin and lower orbital moments than we find in our work. What is more important, however, is that irrespective of the functional that has been used, Fernández-Seivane and Ferrer report much larger spin and orbital anisotropies for both trimers. It appears that the differences in the orbital moments are a consequence of the on-site approximation used for the calculation of the spin–orbit coupling matrix elements within their local orbital approach [64], while the local spin moments are derived from a Mulliken analysis. It has been demonstrated that the Mulliken analysis based on overlapping local orbitals systematically leads to larger local moments than the integration over atomic spheres [38]. The anisotropy in the total magnetic moment per trimer can be as large as 0.88 μB, distributed about equally between spin and orbital contributions. With such a large change in the moment, it appears to be legitimate to raise the question whether their ‘excited state’ really differs from the ground state only by a rotation of the magnetization direction and if it does not rather represent an excited magnetic isomer. If we add the excitation energy for the LM isomer of the Pd3 cluster to our calculated MAE, we arrive at an energy which is very close to the value reported by Fernández-Seivane and Ferrer [32].

### 3.2. Tetramers

According to the scalar-relativistic calculations the ground state of the Ni4 tetramer is a distorted tetrahedron (the point group symmetry is lowered to S4 = 4, with two short edges of 2.20 Å and four long ones of 2.32 Å) and a spin moment of μS = 4 μB and local moments of 1 μB on all four atoms. A Pd4 cluster forms a regular tetrahedron (edge length 2.61 Å, symmetry group Td = 43m) with a magnetic moment of μS = 2 μB. For the calculations including SOC, again three different orientations of the magnetic moment have been chosen for the initial configuration: (i) along the x-axis, i.e. parallel to one of the edges of the tetrahedron (see figure 3), (ii) along the z-axis, i.e. perpendicular to one of the edges of the tetrahedron (this is parallel to a twofold symmetry axis), and (iii) along the [111] direction (for a perfect tetrahedron this would be parallel to a threefold symmetry axis).

While for a Pt4 cluster SOC induces a preference for a flat structure (a rhombus whose short diagonal has almost the same length as one of the edges) [30, 37], for the Ni and Pd tetramers the tetrahedral structure and bond lengths remain unchanged. For Pd4 the structural energy difference between tetrahedron and rhombus is even increased by 40 meV/atom by including SOC. For Ni4 the total energy is found to be stationary for a magnetization perpendicular to the edges of the cluster, aligned along one of the edges of the tetrahedron or parallel to one of the threefold symmetry axes (along the [111] direction), see figures 3(a)–(c). The total magnetic moment of the cluster is μJ = 3.80 μB, i.e. slightly lower than the spin moment resulting from a scalar-relativistic calculation. The reduction of the spin moment is expected because of the existence of a S = 1 isomer with a low excitation energy of 27 meV, while a S = 3 isomer is higher in energy by 130 meV [15]. The admixture of a low-spin state is compensated by a modest orbital moment. The easy magnetization direction is perpendicular to the edge, the hard oriented parallel to an edge. Both spin and orbital moments of the cluster are isotropic within the computational accuracy, and this is also reflected in a small MAE of 0.46 meV/atom. The local orbital moments are slightly canted relative to the spin moments.

The symmetry of the geometric structure is reduced to C2v = mm2, the magnetic point group m′m′2 allows a parallel alignment of the local spin moments and a slight canting of the orbital moments in all three magnetic configurations. For a magnetization oriented along the hard axis, the broken symmetry is reflected by slightly different orbital moments on pairs of atoms (see figure 3(b)), for a magnetization perpendicular to one of the triangular faces the local orbital moment is smaller on the atoms in the plane perpendicular to the magnetization and larger on the fourth atom (see figure 3(c)). For this orientation of the magnetization, the MAE is only 0.11 meV/atom. The total orbital is almost the same for all three configurations.

For the Pd4 cluster calculations, including SOC conserves the perfect tetrahedral symmetry of the geometric structure and the bond lengths, and thus magnetic moments initialized parallel or perpendicular to one of the edges of the tetrahedron (and hence parallel to a twofold symmetry axis) converged to energetically degenerate stationary solutions with spin and orbital moments of μS = 1.84 μB, μL = 0.48 μB, and μJ = 2.32 μB. A slight reduction of the spin moment compared to the scalar-relativistic result is overcompensated by the orbital moment of the cluster. However, as no magnetic point group with tetrahedral symmetry is compatible with a ferromagnetic state [63], magnetization necessarily reduces the symmetry of the cluster. For the easy-axis orientation the MPG is m′m′2, with the total magnetic moment parallel to the twofold
Figure 3. Structure and local magnetic moments of Ni₄ ((a), (b), and (c)) and Pd₄ ((d), (e)) clusters for different orientations of the magnetization direction. Cf figure 2 and the text.

symmetry axis. The size of the local spin and orbital moments is the same on all four sites, the local orbital moments are slightly canted relative to the overall magnetization directions (see figure 3(d)). For a magnetic moment oriented along a threefold symmetry axis the total and local spin moment are the same, but the local orbital moments are now aligned with the spin moments. The local orbital moment is significantly larger on the atom located on the threefold symmetry axis. This leads also to a small enhancement of the cluster orbital moment to $\mu_L = 0.51 \mu_B$. The MPG is 32'. This magnetic axis is disfavored by an MAE of 0.26 meV/atom.

For the Pt₄ cluster, inclusion of SOC not only stabilizes a planar over the tetrahedral structure (in agreement with Huda et al [30] and Xiao and Wang [65], but in disagreement with Sebetci [31]), it also stabilizes an antiferromagnetic ground state [37]. For a tetrahedral Pt₄ cluster a noncollinear antiferromagnetic ground state with the local moments oriented along the four threefold symmetry axes was reported. The geometric structures predicted for Pd₄ and Pt₄ structures agree with the results of Fernández-Seivane and Ferrer [32]. For the Pd₄ tetrahedron these authors report two frustrated noncollinear ferromagnetic configurations to be lower in energy than a noncollinear antiferromagnetic configuration, similar to that reported by Bloński et al [37] for the Pt₄ tetrahedron. In the two energetically most favorable states, a large magnetic moment exists only at one site. A total spin moment of about 1 $\mu_B$ and a modest orbital moment of about 0.2 $\mu_B$ seems to be hard to reconcile with a spin moment from the scalar-relativistic calculations, which, according to the number of valence electrons, can only be zero or an even multiple of $\mu_B$. The energy difference between these two configurations of 3.5 meV/atom has been interpreted as the
MAE of the cluster—this would be one order of magnitude larger than our result.

3.3. Pentamers

For all pentamers the scalar-relativistic calculations predict a trigonal bipyramid (point group symmetry $D_{3h}$) to be the ground-state configuration, with a spin of $S = 2$ for Ni$5$ and Pt$_3$ and $S = 1$ for Pd$_3$, respectively. The lengths of the bonds forming the central triangle of Ni$5$ (2.25 Å) are shorter than the bonds to the atoms at the apices (2.33 Å). In contrast, in the Pd pentamer the bonds forming the triangle are longer (2.91 Å) than the remaining bonds (2.56 Å). However, a structure which is closer to that of the Ni pentamer is almost energetically equivalent. The local magnetic moments of the apical atoms are always slightly lower than those on the atoms forming the central triangle: $0.74/0.84 \mu_B$ and $0.35/0.43 \mu_B$ for Ni$5$ and Pd$3$, respectively.

The calculations including SOC have been initialized with the magnetic axis parallel to the threefold symmetry axis, within the plane of the central triangle, and along the [111] direction. Adding spin–orbit coupling stretches the interatomic distances within the central Ni-triangle by 0.01 Å, the total magnetic moment of the Ni$5$ cluster is $\mu_j = 4.27 \mu_B$, $\mu_S = 3.82 \mu_B$ and $\mu_L = 0.45 \mu_B$ in the magnetic ground state with the easy magnetic axis in the equatorial plane, along a twofold symmetry axis (see figure 4(a)). In the ground-state configuration local spin and orbital moments are strictly collinear, both spin and orbital moments are smaller on the apical atoms. The hard magnetic axis is the threefold symmetry axis. The spin moments are isotropic, the orbital moments are the same on all atoms with $\mu_L = 0.10 \mu_B$, leading to a slight increase of the total orbital moments to $0.50 \mu_B$ (see figure 4(c)). A magnetization perpendicular to the threefold axis reduces the magnetic symmetry to orthorhombic (MPG $m'm'm'$), without inducing a geometric distortion and with only very small differences in the local orbital moments. For the hard magnetic axis parallel to the threefold symmetry axis the MPG is $6m'2'$. The MAE is $0.27$ meV/atom relative to the in-plane orientation, although this configuration has slightly lower orbital moments. The in-plane anisotropy is determined by a rotation of the magnetization by an angle of $60^\circ$ with respect to the twofold symmetry axis of the central equilateral triangle (see figure 4(b)), it amounts to only $0.09$ meV/atom at almost isotropic total spin and orbital moments.

For the Pd$5$ cluster SOC changes the geometry for in-plane magnetization: the equatorial plane forms an isosceles triangle with one bond shorter by 0.03 Å than the remaining two, and the distances between the apical atoms are stretched by about 0.02 Å. The crystallographic symmetry is reduced to $C_{3v} = mm2$. The easy magnetic axis lies in the equatorial plane, in this case we also determine a larger in-plane anisotropy energy than for Ni$5$: a rotation of the magnetization axis by $60^\circ$ leads to an increase of the total energy by $0.91$ meV/atom (see figures 4(d) and (e)). In both cases the MPG is $m'm'm'$.

The cluster moments for in-plane magnetization are $\mu_j = 2.38 \mu_B$, $\mu_S = 1.81 \mu_B$ and $\mu_L = 0.57 \mu_B$; i.e. mixing with low-spin states is overcompensated by the orbital moment. Local orbital moments are slightly canted relative to the local spin moments only on the apical atoms. Rotation of the magnetic axis within the plane leaves the spin moments almost unchanged, but the total orbital moment slightly decreases for the hard in-plane orientation.

Calculations initialized along the threefold axis always relaxed to in-plane orientation of the magnetic moments. Therefore the MAE could only be calculated for a frozen direction of the magnetization parallel to the threefold symmetry axis, resulting in an MAE of $2.1$ meV/atom. For the hard axis the geometric symmetry is conserved, the magnetic symmetry is $6m'2'$. The spin moments are slightly, and the orbital moments are strongly reduced to half of their value calculated for the easy axis (see figure 4(f) for details).

For the Pt$5$ cluster SOC stabilizes a planar structure, rotation of the magnetization axis leads to complex transitions between different magnetic isomers [37]. For the Pt$5$ cluster forming a trigonal bipyramid, the easy axis is again in-plane, the total magnetic moment of the cluster is $\mu_j = 3.69 \mu_B$, with $\mu_S = 2.76 \mu_B$ and $\mu_L = 0.93 \mu_B$, i.e. much larger than for Pd$5$. The hard axis is the threefold symmetry axis. The MAE is rather large, $4.3$ meV/atom [37]. For the Pd$5$ cluster Fernández-Seivane and Ferrer [32] report a stable structure in form of a trigonal bipyramid and similar spin, but lower orbital moments than our calculations. From the Supplementary Information to their paper we find out-of-plane (uniaxial) MAE of $0.4$ meV/atom and a very small in-plane anisotropy of $0.1$ meV/atom, in good agreement with our results. The lower orbital moments in their calculations also lead to the slightly lower value for the MAE.

3.4. Hexamers

For the Ni$6$ cluster the scalar-relativistic calculations predict a slightly distorted octahedral geometry (point group symmetry reduced to $D_{4h} = 4/mmm$) with a spin moment of $8 \mu_B$. The local magnetic moments at the two apical atoms are reduced by $0.02 \mu_B$ compared to those on the four equatorial atoms. The GS structure of Pd$6$ is a non-magnetic perfect octahedron (symmetry group $O_h = m3m$, bond length of 2.65 Å). Previous calculations by Futschek et al [14] for Pd$6$ predicted the $S = 1$ state to be the GS, but note that the $S = 0$ isomer is only $10$ meV/atom higher in energy. For the Pt$6$ cluster a capped square pyramid with $S = 3$ was found to be preferred over a distorted octahedron with the same spin [14].

SOC leaves the geometry of the Ni hexamer unchanged, the total moment per cluster is reduced to $\mu_j = 7.12 \mu_B$ ($\mu_S = 6.54 \mu_B$ and $\mu_L = 0.58 \mu_B$). The easy magnetic axis is parallel to the fourfold symmetry axis, with collinear spin and slightly canted local orbital moments (MPG $4/mmm'$; see figure 5). The local spin moments are almost $1.09 \mu_B/atom$, but large differences are found for the local orbital moments: $0.12 \mu_B$ on the equatorial atoms (canted by $7^\circ$ relative to the spins) and $0.05 \mu_B$ on the apices (canted by $17^\circ$). The hard magnetic axis of Ni$6$ lies parallel to one of the edges of the central square of atoms (i.e. along a twofold symmetry axis). In this configuration the fourfold rotational symmetry is broken, the MPG is $mm'm'$. The local spin moments of $1.09 \mu_B/atom
are completely isotropic, but the local orbital moments on the four equatorial sites are reduced to 0.09 \( \mu_B/\text{atom} \) (canted by \( \pm 24^\circ \) relative to the spins), and those on the apical atoms are enhanced to 0.13 \( \mu_B/\text{atom} \) and collinear to the spins. The MAE is only 0.21 meV/atom. A stationary state is also found for a magnetic axis perpendicular to one of the triangular facets (for a perfect octahedron this would be a threefold symmetry axis). The energy of this configuration is only 0.1 meV lower than for magnetization along the hard axis.

Applying SOC to the calculation for the Pd\(_6\) octahedron promotes a magnetic GS structure with a cluster moment of \( \sim 2.6 \mu_B \) (\( \mu_S = 1.90 \mu_B \) and \( \mu_L = 0.66 \mu_B \)). A Jahn–Teller distortion lowers the symmetry to \( D_{4h} \), the interatomic distances between the central square are stretched to 2.69 Å, and those to the apical atoms are unchanged. This is reflected in the local moments: the four equatorial sites carry local spin moments of 0.28 \( \mu_B/\text{atom} \) and very small local orbital moments of 0.03 \( \mu_B/\text{atom} \), whereas on the apical atoms...
both the local spin and orbital moments are enhanced to 0.39 and 0.27 \( \mu_B \)/atom, respectively. The magnetic moments are strictly aligned (compare figures 5(c) and (d)). The MPG is \( 4/mm'm' \), as for the Ni\(_6\) cluster. Similarly as for Ni\(_6\), the hard magnetic axis of Pd\(_6\) lies parallel to one of the edges of the equatorial square, the magnetic symmetry is reduced to \( mm'm' \). A rotation of the magnetization direction from the easy to the hard magnetic axis inverts both the geometry of the cluster (the bonds between equatorial atoms are shortened to 2.63 Å, while those to the apical atoms are stretched to 2.68 Å) and the relative size of the local magnetic moments (now, the local moments on the apical atoms are reduced, whereas those on the four equatorial sites are increased and canted by \( \pm 21^\circ \)).

For Pt\(_6\) the relativistic calculations reverse the energetic order in favor of the perfect octahedron with bond lengths of 2.62 Å [37]. In the GS, the magnetic structure of the Pt\(_6\) cluster is rather complex, with strongly noncollinear local spin and orbital moments (local spins are oriented along the square diagonals, while the local orbital moments are aligned along the edges and they are antiparallel and slightly deviate from the equatorial plane). The cluster total moment, oriented perpendicular to one of the triangular facets, is low \( \mu_J = 0.83 \mu_B \). The hard magnetic axis is aligned along one of the edges of the equatorial square with an MAE of 1.4 meV/atom.

Fernández-Seivane and Ferrer [32] reported results only for Pd\(_6\). Geometry and bond lengths agree reasonably with our results, but the tetragonal distortion of the octahedron is less pronounced. The GS is almost non-magnetic, with a spin moment of only 0.036 \( \mu_B \) and a larger orbital moment of 0.148 \( \mu_B \). Their MAE of about 1 meV/atom is calculated for a non-magnetic excited state. We believe that the differences in magnetic moment and total energy represent rather the computational accuracy of their set-up rather than a true magnetic anisotropy.

### 3.5. 13-atom clusters

For a cluster formed by 13 atoms it is generally expected that the equilibrium structure is an icosahedron, because this structure allows for the formation of the maximum...
number of nearest-neighbor bonds. Recent studies [12, 14–23] have demonstrated that this is not the case, without, however, converging to a generally accepted result. These calculations have been performed using different \textit{ab initio} codes: VASP [12, 14–17, 21], SIESTA [18, 19], or GAUSSIAN03 [20, 21] and using either plane-wave (VASP) or localized (SIESTA, GAUSSIAN03) basis sets, pseudo-potentials (SIESTA) or all-electron (GAUSSIAN03, VASP) methods (note that the projector-augmented wave method implemented in VASP uses the full electron density and hence should be considered as an all-electron method). While these technical differences may account for some quantitative differences in the structural energy differences, the main origin of the discrepancies in the predicted ground-state configurations is probably in the algorithms used in searching for the global energy minimum. Futschek \textit{et al} [14, 15] used a dynamical simulated annealing strategy starting with a high-temperature molecular-dynamics run, followed by a slow-cooling process and a final static conjugate-gradient minimization. Wang and Johnson [16] followed a procedure originally proposed by Stillinger and Weber [70, 71] for generating low-energy amorphous structures. During a high-temperature MD run, low-energy configurations are monitored, and these selected configurations are optimized by a static minimization. Kumar and Kawazoe [17] built the structure of larger clusters by sequentially adding atoms to the structures of low-energy isomers of smaller clusters. Aguilera-Granja \textit{et al} [18, 19] use static relaxations starting from clusters with different symmetries. Fournier \textit{et al} [20–22] used a search algorithm called ‘taboo search in descriptor space’ [72] attempting to interpolate in configuration space between local energy minima detected in DFT calculations using appropriately chosen descriptors, and to search for novel candidate structures.

For the Ni\textsubscript{13} cluster the first calculations of Aguilera-Granja \textit{et al} [18] predicted an icosahedral structure with a moment of 8 \(\mu_B\) to be the ground state, in good agreement with Futschek \textit{et al} [15], who found a distorted icosahedron with the same magnetic moment. More recent calculations of Aguilera-Granja \textit{et al} [19] reported a structure in the form of a ‘fragment of a double icosahedron’ and a higher moment of 10 \(\mu_B\). However, no structural or magnetic energy differences with respect to the previously reported structure are given. For Pd\textsubscript{13}, Chang and Chou [12] and Futschek \textit{et al} [14] reported a GS structure forming a biplanar arrangement of close-packed layers and a magnetic moment of 6 \(\mu_B\), Wang and Johnson [16] a low-symmetry structure with the same moment (but a slightly different biplanar structure was found to be only 5 meV/atom higher in energy). Aguilera-Granja \textit{et al} [18, 19] reported the same conflicting results as for Ni\textsubscript{13}. Fournier \textit{et al} [20, 21] found distorted icosahedral structures with a magnetic moment of 8 \(\mu_B\), but the character and magnitude of the distortion were not specified. It also appears that their ‘global’ search algorithm did not explore layered configurations. For Pt\textsubscript{13} Futschek \textit{et al} [15] reported a similar, but non-magnetic, biplanar structure as for Pd\textsubscript{13}. Wang and Johnson [16] found that the GS is a ‘double triangle’ structure with a magnetic moment of 2 \(\mu_B\), which is essentially a different stacking variant of the biplanar structure reported by Futschek \textit{et al}. Kumar and Kawazoe [17] reported a triangular bilayer structure with a capping atom in a threefold site and \(\mu = 2 \mu_B\), similar to Wang and Johnson. Aguilera-Granja \textit{et al} reported first [18] an icosahedral GS, and later [19] a structure similar to that reported by Kumar and Kawazoe. Fournier \textit{et al} reported a structure for Pt\textsubscript{13} described as an ‘oblate multiply capped trigonal prism’ (which we would consider rather as a kind of square pyramid) which is characterized either as non-magnetic [22] or weakly magnetic (\(\mu = 2 \mu_B\)) [20]. The problem is that the results are difficult to compare—even when results for a large number of isomers are reported, the structures dealt with in the other studies cannot be found among them. The MD + static relaxation approach used by Wang and Johnson [16] seems to be able to explore the largest region of configuration space, but one has to keep in mind that the static optimization always converges to a minimum of the static potential energy connected to a selected high-temperature minimum by a steepest descent path—it is not evident that this will allow one to detect the global minimum. The simulated annealing approach used by Futschek \textit{et al} [14, 15] depends on the quenching speed—which is always too high. The search algorithm of Fournier \textit{et al} [72] seems to look preferentially for three-dimensional structures. A comparison of accurate total energies could decide the issue, but at the level of the structural energy differences in question, energies derived from different codes cannot be directly compared, and even if the same code has been used, the results depend on basis set completeness (cut-off energies for plane-wave codes), convergence criteria for forces and energies etc which are hardly ever reported in sufficient detail.

An alternative is to compare the structural energy differences relative to a common reference configuration, for example an ideal icosahedron. For a Ni\textsubscript{13} cluster there is good agreement between the structural energy differences of a cuboctahedron of 92(88) meV/atom and of a buckled biplanar structure of 10(10) meV/atom relative to an ideal icosahedron calculated by Futschek \textit{et al} [14] and Piotrkowski \textit{et al} [23] (results in parentheses). Equilibrium magnetic moments of 8 \(\mu_B\) for the icosahedron and 10 \(\mu_B\) for the biplanar structure are also in agreement. The relaxation of the icosahedron (lowering the symmetry to C\textsubscript{1h}) leads to an energy gain of 21 meV/atom, which is more than the 10 meV/atom for the lowest energy structure detected by the global search algorithm of Piotrkowski \textit{et al}. Hence the distorted icosahedron is confirmed as the equilibrium structure of the Ni\textsubscript{13} cluster.

For Pd\textsubscript{13} we find that the buckled biplanar structure is lower in energy by 26 meV/atom than the ideal icosahedron. The energy difference for the asymmetric lowest energy structure of Piotrkowski \textit{et al} [23] is 25 meV/atom, for the structure reported by Wang and Johnson [16] it is 22 meV/atom. All three calculations agree in a total magnetic moment of 8 \(\mu_B\) for the icosahedron and 6 \(\mu_B\) for the optimal structure. Hence for Pd\textsubscript{13} we can only conclude that the energy surface in configuration space is very flat, with multiple minima differing only by a few meV/atom.

For Pt\textsubscript{13} the situation is different. Relative to an ideal icosahedron with a moment of 2 \(\mu_B\) the energy of
a buckled biplanar structure with zero moment is lower by 165 meV/atom (present work) and 160 meV/atom [16], respectively. Piotrkowski et al [23] report an energy difference of 154 meV/atom for a slightly different biplanar configuration with a moment of 4 μB. The good agreement shows that the comparison of the structural energy differences is meaningful. Both studies report low-energy structures which have not been detected using the dynamical simulated annealing strategy of Futschek et al [14]. The energetically most favorable structure of Wang and Johnson [16], with a moment of 2 μB, is lower in energy by 240 meV/atom, Piotrkowski et al [23] reported a structure with the same moment and an even larger energy difference of 271 meV/atom.

3.5.1. Ni13. For the Ni13 cluster the scalar-relativistic calculations predict for the distorted icosahedron with 8 μB an excitation energy for a low-spin isomer with a ferrimagnetic structure (opposite orientation of the magnetic moment on the atom in the center) of only 24 meV/atom. This excitation energy is only slightly lower than the structural energy difference of 31 meV/atom with respect to the biplanar arrangement. The symmetry of this configuration has been described as C1h, but the distortion from a threefold symmetry (point group C3v = 3m) with respect to an axis perpendicular to the close-packed planes is only minimal. Magnetic isomers with moments of 10 and 12 μB are almost degenerate in energy, the local moments reflect the approximate threefold symmetry with respect to an axis perpendicular to the planes [15]. A third metastable structural variant consists of a centered distorted cube, capped on four square facets such that the point group symmetry is D4h = 4/mmm. This configuration has spin S = 5, and it is higher in energy by 71 meV/atom than the distorted icosahedron.

For the Ni13 cluster the fully relativistic calculations confirm the icosahedral ground-state geometry with unchanged interatomic distances. The structural energy difference is slightly enhanced for the capped cube and unchanged for the biplanar structure. For the distorted Ni13 icosahedron we have found local equilibria for the magnetization oriented along a pseudo-threefold or a pseudo-fivefold symmetry axis—the former is the easy and the latter the hard magnetic axis (see figure 6). The distortion of the geometric structure is also reflected in small differences in the local spin and orbital moments, in the magnetic state the mirror symmetry is broken, the MPG is only 1. The MAE is 0.4 meV/atom. A calculation initialized along a twofold symmetry axis also converged to the same easy axis. For this orientation the total magnetic moment is μJ = 8.97 μB (μS = 8.48 μB and μL = 0.49 μB). The spin moment is found to be isotropic, but for the hard magnetic axis we calculate a larger orbital moment of μL = 0.82 μB. Both the spin and orbital moments on the atom in the center of the icosahedron are reduced by about a factor of two compared to those on the outer vertices. Local spin moments vary between 0.63 and 0.73 μB, and local orbital moments between 0.03 and 0.05 μB for easy-axis, and between 0.04 and 0.08 μB for hard-axis magnetization, and most local orbital moments are canted relative to the local spin moments by angles up to 28°. For the structural isomer forming a centered, capped cube slightly elongated along the tetragonal axis, the structural energy difference is slightly increased from 71 to 93 meV/atom. The easy magnetic axis is parallel to the fourfold symmetry direction of the geometric structure (see figure 6(c)). Due to small differences in the canted local orbital moments, the MPG is reduced to m′, with the mirror plane parallel to the (x, y)-plane. The in-plane anisotropy is very small, only 0.06 meV/atom. In the configuration with the global magnetization direction along the x-axis a higher magnetic symmetry (MPG m′m′2) with the twofold axis parallel to the magnetization is conserved. The hard axis is perpendicular to the fourfold symmetry axis (y-direction). In this configuration the MPG is reduced to m′, the MAE is 0.6 meV/atom. As expected, the mixing with low-spin states leads to a reduction of the magnetic moment relative to the spin moment of 10 μB found in the scalar-relativistic calculations, to μJ = 7.03 μB, μS = 6.14 μB and μL = 0.90 μB. The spin moment is isotropic, but the orbital moments differ by ΔμL = 0.4 μB. On the atom in the center of the cube, the spin moment is reduced and aligned antiparallel to that on the outer sites, and the local orbital moments are completely quenched (to a value smaller than 0.01 μB). Local orbital moments are canted relative to the local spin moments, which are aligned relative to the chosen magnetic axis.

The structural energy difference of 31 meV/atom found for the biplanar structure relative to the icosahedron is unaffected by SOC. If the direction of magnetization is initialized parallel to the atomic planes, the direction of the moments is found to be locally stable, (see figure 6(f)), with a total cluster moment of μJ = 12.48 μB (μS = 11.39 μB and μL = 1.09 μB), i.e. comparable to the spin moment from the scalar-relativistic calculations. The magnetization reduces the symmetry to a mirror operation perpendicular to the global magnetic moment, the MPG m is compatible with the canting of the local orbital moments. If the direction of magnetization is initialized perpendicular to the atomic planes, it relaxes to an oblique orientation with unchanged spin and orbital moments. A calculation with frozen perpendicular magnetization leads to a configuration with conserved threefold symmetry (MPG 3), the MAE is 0.09 meV/atom. The spin moment is isotropic, the orbital moment is reduced from 1.23 μB to 1.09 μB.

Our result for the Ni13 icosahedron can be compared with the results of Sahoo et al for icosahedral Fe, Co, and Ni clusters [38]. If an ideal icosahedral symmetry is enforced, a Ni13 cluster has an MAE of only 0.77 μeV/atom. Only a restricted relaxation describable by one-parameter models has been permitted: a ‘Jahn–Teller (JT) distortion’ preserving the fivefold symmetry, but contracting the cluster along the fivefold axis, and a ‘Mackay (M) distortion’ reducing the point group symmetry from icosahedral to tetrahedral and initiating a transformation of the icosahedron into a cuboctahedron. For Ni13, both JT and M relaxations lead to an energy gain of about 16 meV/cluster compared to an ideal octahedron. This is slightly smaller than the lowering of the total energy by 21 meV/atom upon unconstrained relaxation. The average values for the spin and orbital moments per atom (0.66 μB and 0.06 μB, respectively) are very close to our values, and
Figure 6. Geometric and magnetic structures of Ni$_{13}$ clusters: the top row shows the icosahedral ground-state configurations, with the magnetization oriented along a threefold (a) and a fivefold (b) symmetry axis. The former is the easy magnetic axis. The second row shows the structure consisting of a centered cube capped on four square facets, with the magnetization directed along one of the Cartesian axes ((c)–(e)). The easy axis is the $y$-direction parallel to the fourfold symmetry axis (d), the hard axis in the $z$-direction (e). The bottom row shows the biplanar structure, with the magnetization initialized along the $x$ and $z$ directions, i.e. parallel and perpendicular to the close-packed planes ((f), (g)). Spin moments are shown by the red arrows, orbital moments by the blue arrows. For sake of clarity, the length of the arrows representing the orbital moments has been multiplied by ten. Cf figure 2 and the text.

also very close to the bulk values. No information on the anisotropy of the magnetic moments is given in their work. For a JT-distorted Ni$_{13}$ icosahedron, an MAE of 0.688 meV/atom was reported. This MAE is about 30 times larger than that calculated for the M-distorted cluster. The MAE for the JT-distorted cluster is of the same order of magnitude as our result, although the full relaxation leads to a much lower symmetry.

3.5.2. Pd$_{13}$. For the Pd$_{13}$ cluster the buckled biplanar arrangement with a magnetic moment of 6 $\mu_B$ represents the GS, and the cluster now has perfect $C_{3v} = 3m$ symmetry (although this has been overlooked in the earlier work [14]). The magnetic energy difference from the LM (4 $\mu_B$) isomer is only 3 meV/atom, and rises to 22 meV/atom for the HM (8 $\mu_B$) magnetic isomer, reaching a value comparable to the structural energy difference with respect to a perfect icosahedron (symmetry $I_h$, magnetic moment 8 $\mu_B$) of 26 meV/atom. The structural energy difference of a capped cube with a central atom (symmetry $D_{4h} = 4/mmm$, magnetic moment 4 $\mu_B$) is almost twice as large at 39 meV/atom [14].
The calculations including SOC for Pd$_{13}$ confirm the biplanar structure to be the ground state, but the structural energy difference with respect to the icosahedron is reduced to 13 meV/atom, whereas that of the capped cube is increased to 57 meV/atom. The modest influence of SOC on the structural energy differences is in agreement with Piotrkowski et al [23], who did not report any magnetic data from their relativistic calculations. The easy magnetic axis is perpendicular to the atomic planes, the total magnetic moment of the cluster is $\mu_J = 7.13 \mu_B$ ($\mu_S = 5.41 \mu_B$, $\mu_L = 1.72 \mu_B$), the orbital moment leads to an increased magnetization compared to the scalar-relativistic limit. In this configuration, threefold symmetry (MPG 3) is conserved (see figure 7(a)). The hard axis lies parallel to the atomic planes, breaking the threefold symmetry (MPG 1). The MAE is 0.28 meV/atom. The small MAE is reflected in a low spin and orbital anisotropy: $\Delta \mu_S = 0.20 \mu_B$ and $\Delta \mu_L = -0.06 \mu_B$. For both magnetization axes, local spin and orbital magnetic moments are slightly noncollinear (see figure 7).

It is remarkable that, while for the smaller clusters, from trimer to hexamer, the easy magnetic axis is always the same for Ni and Pd clusters, for the biplanar 13-atom clusters the easy axis is in-plane for Ni and perpendicular for Pd. Different orientations of the magnetic moment in the GS have been reported for the Ni and Pd dimers [36], where they could be attributed to the different electronic configuration of the atoms.

Any initialization of a magnetization direction for the remaining Pd$_{13}$ structures always converges to the easy magnetic axis, for the icosahedron parallel to a fivefold symmetry axis, and for the capped cube parallel to the fourfold symmetry axis.

3.5.3. Pt$_{13}$. For the Pt$_{13}$ cluster we have examined the buckled biplanar structure with $C_{3v} = 3m$ symmetry found by Chang and Chou [12] and Futschek et al [14], as well as the lowest energy structure identified by Wang and Johnson [16]. This structure is also a biplanar arrangement, but with two triangular fragments of a close-packed plane with six atoms each stacked exactly one above the other, with the 13th atom located in a threefold hollow. Wang and Johnson reported several such triangular biplanar structures, which differ only in the location of the 13th atom and which are all lower in energy than the buckled biplanar structure. A 13-atom cluster also represents the upper size-limit for a spontaneous magnetic polarization of Pt clusters: the biplanar cluster has a non-magnetic ground state (but very low excitation energies for states with $S = 1–4$), the ground state of the lowest energy structure, as well as that of a distorted icosahedron and a distorted cubic structure has spin $S = 1$, again with low excitation energies for low- and high-spin states.

Calculations including SOC and admitting a noncollinear magnetic structure converge for the biplanar structure to a magnetic state with locally fluctuating spin and orbital moments, adding to modest cluster moments of $\mu_J = 1.47 \mu_B$ ($\mu_S = 0.88 \mu_B$ and $\mu_L = 0.64 \mu_B$), quite independent of the initialization. The distribution of the local moments breaks the threefold symmetry (see figure 8). No clear preference for a magnetic easy axis could be detected. This corresponds to the scalar-relativistic fixed-moment result of energetically degenerate $S = 1$ and 0 isomers.

For the lowest energy triangular structure we have initialized the magnetization along a direction perpendicular
to the two atomic layer, and along two perpendicular in-plane directions. For a perpendicularly magnetized the calculations converge to a non-magnetic state—this is also the ground state. If the magnetization is initially set along the x-direction (see figure 9), along one of the edges of the triangle we find a slightly noncollinear magnetic configuration (absolute values of total, spin and orbital moment $\mu_J = 1.58 \mu_B$, $\mu_S = 1.06 \mu_B$, $\mu_L = 0.52 \mu_B$) which is only 0.08 meV/atom above the ground state. The magnetic point group symmetry is $m'$. Initialization along a direction parallel to the mirror plane of the structure (along the y-direction) leads to a noncollinear magnetic configuration with lower moment ($\mu_J = 0.92 \mu_B$, $\mu_S = 0.68 \mu_B$, $\mu_L = 0.25 \mu_B$). The in-plane MAE is 1.03 meV/atom.

For the distorted icosahedron we calculate a similar magnetic configuration, with slightly larger spin ($\mu_S = 1.67 \mu_B$) and lower orbital ($\mu_L = 0.23 \mu_B$) moments and a stronger canting between local spin and orbital moments. The difference between both structural isomers corresponds to a slightly larger scalar-relativistic energy difference between the icosahedral spin isomers, with a preference for the a structure. The magnetic point group symmetry is $m$. Initialization along a direction parallel to the mirror plane of the structure (along the y-direction) leads to a noncollinear magnetic configuration with lower moment ($\mu_J = 0.92 \mu_B$, $\mu_S = 0.68 \mu_B$, $\mu_L = 0.25 \mu_B$). The in-plane MAE is 1.03 meV/atom.

4. Discussion

We have performed a first-principles investigation of the influence of spin–orbit coupling on the structural and magnetic properties of small transition-metal clusters formed by Ni and Pd, completing our investigation of the MAE of clusters of the Pt-group elements. For Pt clusters we had found that SOC can reverse the relative stability of structural isomers (and in particular stabilize planar structures for Pt₄ and Pt₅ clusters) and lead to a large MAE comparable to the energy difference between magnetic isomers. In contrast, SOC does not affect the relative stability of different structural isomers of Ni and Pd clusters, although it can lead to modest changes in the interatomic distances and induce changes in the crystallographic and magnetic point group symmetries, depending on the orientation of the magnetization axis.

The quantities of central interest to our investigation are the orbital magnetic moment and the magnetic anisotropy of the clusters. The results are summarized in table 1, including our previous results for Pt clusters [37] and on dimers of all three elements [36]. Both the orbital moment and the MAE are found to depend on the strength of the SOC, the size and the geometry of the cluster. For the Ni₂ clusters the mixing of different spin states caused by the coupling to the orbital moment leads to a reduction of the spin moment (with the exception of the trimer), the orbital moment is approximately 0.5 $\mu_B$/cluster, varying only little with cluster size and leading to a rapidly decreasing $\mu_L/\mu_S$ ratio with increasing cluster size. The total magnetic moment per cluster varies between $\mu_J = 2.77 \mu_B$ for the trimer and $\mu_J = 8.97 \mu_B$ for the icosahedron, the moment per atom varies around 1 $\mu_B$ for the small clusters and reaches 0.69 $\mu_B$ for the icosahedron, a value close to that in bulk Ni. The spin moment is generally isotropic, a substantial orbital anisotropy of either sign is found only for the Ni dimer and trimer ($\Delta \mu_L = 0.2 \mu_B$ and 0.4 $\mu_B$, respectively) and for the distorted Ni-icosahedron ($\Delta \mu_B = -0.33 \mu_B$).

Pd clusters differ from Ni and Pt by a different electronic ground state ($s^2d^{10}$ instead of $s^1d^9$). Hence, Pd clusters have a lower binding energy than both Ni or Pt clusters, because bond formation requires an opening of the closed d⁹ shell. An open d shell is also required for the formation of a magnetic moment. The Pd₂ dimer has a spin moment of ∼2 $\mu_B$ and an almost vanishing orbital moment, clusters with $n = 2–6$ have a small spin moment increasing from 1.66 $\mu_B$ to 1.90 $\mu_B$ and an orbital moment varying between 0.93 $\mu_B$ and 0.48 $\mu_B$, resulting in an almost constant total magnetic moment per cluster of $2.45 \pm 0.1 \mu_B$ and a ratio $\mu_L/\mu_S$ decreasing only slowly from about 0.6 for the trimer to 0.3 for the hexamer. Pd clusters show a very small spin anisotropy and a much larger orbital anisotropy of either sign—except the Pd₄ tetrahedron with isotropic spin and almost isotropic orbital moment. For the larger Pd₁₃ cluster with a planar structure the spin moment (5.4 $\mu_B$) is much larger and more anisotropic than the orbital moment (1.7 $\mu_B$).

For Pt clusters the situation is very complex [37]. Dimer and trimer have a ferromagnetic ground state with $\mu_J = \mu_S = \mu_L = 0.08 \mu_B$.
among the dimers, Ni2 and Pt2 have an easy magnetization depending on electron configuration, SOC and symmetry. A weak magnetic moment can be induced by a rotation of the magnetic axis. A weak magnetic transition. In the stable triangular geometry the GS is weakly magnetic in a scalar-relativistic treatment, but non-magnetic if SOC is taken into account. A weak magnetic moment can be induced by a rotation of the magnetic axis.

Trends in the magnetic anisotropy are very complex, depending on electron configuration, SOC and symmetry. Among the dimers, Ni2 and Pt2 have an easy magnetization direction along the dimer axis, while Pd2 shows perpendicular anisotropy. As discussed in detail before [36], the difference arises from the different character of the states closest to the Fermi level and hence from the different electronic configurations of the free atoms. All trimers have an easy axis within the plane defined by the three atoms. For Ni3 and Pd3 the threefold symmetry is reduced in the GS (magnetic point group 2m’m’), but preserved for perpendicular magnetization. The lower MAE of the Pd3 trimer arises from the different sign in the spin and orbital anisotropies. For Pt3 the same reduced symmetry is also found for perpendicular orientation, both spin and orbital moments are larger for the in-plane GS. For the Ni4 cluster the tetrahedral symmetry is broken for the geometric as well as the magnetic structure (MPG 432), irrespective of the direction of magnetization. For Pd4 the tetrahedral crystallographic symmetry is conserved, but the magnetic symmetry is reduced to m’m’2 for the easy and to 32’ for the hard magnetization axis. The Pt4 tetrahedron has a noncollinear antiferromagnetic GS. Note that no tetrahedral magnetic point group is compatible with a ferromagnetic alignment of the local moments. For Ni4 and Pd4 the ratio between the modest MAEs calculated for magnetizations parallel to the twofold and (pseudo)threefold axes is the same as that between the small orbital anisotropies.

Table 1. Equilibrium geometry, magnetic point group symmetry (MPG) for easy and hard magnetization axis, magnetic anisotropy energy MAE (in meV/atom), spin- and orbital anisotropies, \( \Delta \mu_S \) and \( \Delta \mu_L \) (in \( \mu_B \)), and ratio of orbital and spin moments \( \mu_L/\mu_S \) for Ni3, Pd3, and Pt4 clusters. If \( \Delta \mu_{S,L} \) is positive, larger moments are found for the easy-axis orientation. The results for dimers are quoted after [36], for Pt clusters after [37].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Easy (MPG)</th>
<th>Hard (MPG)</th>
<th>MAE</th>
<th>( \Delta \mu_S )</th>
<th>( \Delta \mu_L )</th>
<th>( \mu_L/\mu_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt Dimer</td>
<td>Axial</td>
<td>Perpendicular</td>
<td>3.2</td>
<td>0.02</td>
<td>0.20</td>
<td>0.29</td>
</tr>
<tr>
<td>Pt Dimer</td>
<td>Perpendicular</td>
<td>Axial</td>
<td>-1.1</td>
<td>0.02</td>
<td>-0.34</td>
<td>0.18</td>
</tr>
<tr>
<td>Pt Dimer</td>
<td>Axial</td>
<td>Perpendicular</td>
<td>23.1</td>
<td>0.54</td>
<td>1.94</td>
<td>0.49</td>
</tr>
<tr>
<td>Pd Triangle</td>
<td>In-plane m’m’2</td>
<td>Perpendicular 6m’2’</td>
<td>2.3</td>
<td>0.00</td>
<td>0.40</td>
<td>0.26</td>
</tr>
<tr>
<td>Pt Triangle</td>
<td>In-plane m’m’2</td>
<td>Perpendicular 6m’2’</td>
<td>0.9</td>
<td>0.08</td>
<td>0.19</td>
<td>0.56</td>
</tr>
<tr>
<td>Pt Triangle</td>
<td>In-plane m’m’2</td>
<td>Perpendicular m’m’2</td>
<td>4.4</td>
<td>0.72</td>
<td>0.88</td>
<td>0.99</td>
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<tr>
<td>Ni Tetrahedron</td>
<td>Perpend. edge m’m’2</td>
<td>Parall. edge m’m’2</td>
<td>0.5</td>
<td>0.00</td>
<td>0.02</td>
<td>0.10</td>
</tr>
<tr>
<td>Pd Tetrahedron</td>
<td>Perpend. edge m’m’2</td>
<td>Threefold axis 32’</td>
<td>0.3</td>
<td>0.00</td>
<td>0.01</td>
<td>0.26</td>
</tr>
<tr>
<td>Pt Tetrahedron</td>
<td>Noncoll. AFM</td>
<td>33 2m’ 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni Bipyramid</td>
<td>In-plane m’m’2</td>
<td>Threefold axis 6m’2’</td>
<td>0.3</td>
<td>0.00</td>
<td>-0.05</td>
<td>0.13</td>
</tr>
<tr>
<td>Pd Bipyramid</td>
<td>In-plane m’m’2</td>
<td>Threefold axis 6m’2’</td>
<td>2.1</td>
<td>0.03</td>
<td>0.33</td>
<td>0.31</td>
</tr>
<tr>
<td>Pt Bipyramid</td>
<td>In-plane m’m’2</td>
<td>Threefold axis 6m’2’</td>
<td>4.3</td>
<td>0.12</td>
<td>-0.24</td>
<td>0.34</td>
</tr>
<tr>
<td>Ni Octahedron</td>
<td>Fourfold axis 4/mm’m’</td>
<td>In-plane mm’m’</td>
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<td>0.00</td>
<td>-0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>Pd Octahedron</td>
<td>Fourfold axis 4/mm’m’</td>
<td>In-plane mm’m’</td>
<td>0.3</td>
<td>0.02</td>
<td>-0.10</td>
<td>0.35</td>
</tr>
<tr>
<td>Pt Octahedron</td>
<td>Noncoll. FI 22’22’</td>
<td>Fourfold axis 22’22’</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ni Icosahedron</td>
<td>Threefold axis 1</td>
<td>Fivefold axis 1</td>
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<td>0.00</td>
<td>-0.33</td>
<td>0.06</td>
</tr>
<tr>
<td>Ni Biplanar</td>
<td>In-plane m’</td>
<td>Perpendicular 3</td>
<td>0.09</td>
<td>0.00</td>
<td>0.18</td>
<td>0.10</td>
</tr>
<tr>
<td>Pd Biplanar</td>
<td>Perpendicular 3</td>
<td>In-plane 1</td>
<td>0.3</td>
<td>0.20</td>
<td>-0.06</td>
<td>0.32</td>
</tr>
</tbody>
</table>

4.6(2.5) \( \mu_B \) and \( \mu_L/\mu_S = 1.5(0.7) \) for Pt2 (Pt3), respectively. A Pt4 cluster has an antiferromagnetic GS for both planar and tetrahedral structural isomers. For the planar Pt3 cluster, ferro- and antiferromagnetic states are very close in energy, only the less stable three-dimensional isomers have a ferromagnetic GS with substantial spin and orbital moments. Similarly, for Pt4 a stable octahedral isomer with a low-moment GS coexists with high-moment, but less stable structures. A Pt13 cluster is close to the magnetic \( \rightarrow \) non-magnetic transition. In the stable triangular geometry the GS is weakly magnetic in a scalar-relativistic treatment, but non-magnetic if SOC is taken into account. A weak magnetic moment can be induced by a rotation of the magnetic axis.
anisotropy are much more complex than is usually assumed. The MAE between the hard magnetization direction along the threefold axis and the easy direction in the equatorial plane is 0.3/2.1/4.3 meV/atom for Ni5/Pd5/Pt5, i.e. it increases as naively expected from an increasing strength of the SOC. However, the situation is more complex: the spin moments are isotropic for Ni5 and weakly anisotropic for Pd5 and Pt5, the orbital anisotropy is negative for the Ni and Pt clusters, but positive for the Pd cluster.

The octahedron is the GS geometry for all three hexamers—but note that for the Pt6 cluster this structure is stabilized only by SOC. For Ni6 and Pd6 the symmetry is reduced to tetragonal (MPG 4/m’m’m’) for the easy axis parallel to the fourfold axis. The symmetry is reduced to orthorhombic (MPG mmm’) for the hard axis perpendicular to the rotational axis. The spin moments are almost isotropic, the orbital moments show a modest negative anisotropy. For Pt6 the magnetic symmetry is further reduced to 2/m, 222, the magnetic ground state is noncollinear, with a net magnetic moment oriented perpendicular to one of the triangular facets of the cluster.

For the 13-atom clusters the GS structure is only for Ni13 a distorted icosahedron whose symmetry is further reduced in the magnetic state. The MAE between hard and easy magnetization directions parallel to the three- and fivefold symmetry axes of the idealized icosahedral structure is 0.4 meV/atom, the orbital anisotropy is negative. Pd13 clusters form a biplanar structure which is also metastable for Ni13. Ni and Pd clusters with this structure have high-moment GS, a Pt cluster is only marginally magnetic. The easy magnetic axis of the biplanar clusters is in-plane for Ni (MAE 0.09 meV/atom) and perpendicular for Pd (MAE = 0.28 meV/atom). The Ni13 cluster has isotropic spin moments and a positive orbital anisotropy of 0.14 μB, the Pd13 cluster has a positive, but a weak negative orbital anisotropy. For Pt13 our new calculations confirm that indeed the structure proposed by Wang and Johnson [16] and Kumar and Kawazoe [17] is much lower in energy than either the icosahedron or the buckled biplanar structure. The lowest energy structure is again a biplanar arrangement, but with a different stacking of the two close-packed planes. We find that a Pt cluster of this size is only marginally magnetic—the stable structure is nonmagnetic in the ground state, but with a solution of non-vanishing moments parallel to the atomic planes is essentially degenerate in energy.

Our results show that the factors influencing the magnetic anisotropy are much more complex than is usually assumed. Although only for small Ptn clusters the influence of SOC is strong enough to change the energetic ordering of different structural isomers, even for the lighter Pd and Ni clusters SOC induces magneto-structural effects depending on the direction of magnetization: changes in the magnetic point group symmetries are accompanied by modest geometric distortions of the clusters. The only exceptions are the tetramers where the geometric structure is invariant under rotations of the magnetization direction. For Ni4 clusters the tetrahedral symmetry is broken already at the scalar-relativistic level by a Jahn–Teller distortion, for Pd4 the crystallographic symmetry is preserved, but the magnetic symmetry is reduced, because no tetrahedral point group is compatible with a ferromagnetic state. Rotational symmetry is incompatible with ferromagnetic order between moments perpendicular to the symmetry axis.

Using perturbation theory, a formula relating the MAE to the product of the SOC strength and the orbital anisotropy has been proposed [49]. The derivation of this relation assumes isotropic spin moments (and implicitly also a geometric structure independent of the magnetization direction) and a completely filled majority band, and postulates that the largest orbital moment is always found for easy-axis magnetization. Our results demonstrate that, at least for the heavier elements, the spin moments are never isotropic and that the largest orbital moment is not always found for easy-axis magnetization. For the tetrahedral Ptn and the planar Ptn clusters different initial directions of the magnetization converge to different (ferro-/antiferromagnetic) configurations [37]. In any case these results demonstrate that, for these clusters, the changes in the electronic and magnetic structures induced by a re-orientation of the magnetization axis are too important to be describable by perturbation theory.

Finally we should also point out that our approach shares a certain deficit inherent to all density-functional treatments of orbital polarization: because the calculation of the exchange-field coupling to the magnetic moment is based on averaged charge- and spin-densities, its orbital dependence is underestimated. Hence the orbital moments derived from density-functional theory are always somewhat too small. A coupling between the magnetic moments and the orbital degrees of freedom can, in principle, be achieved within the framework of current spin-density-functional theory, which has achieved some success in predicting the SOC-induced band splitting in semiconductors [66, 67]. For open-shell systems, however, the differences in the results achieved with conventional spin-polarized DFT and current spin-density functionals within an optimized effective potential (OEP) framework were found to be only minimal [67, 68]. Hence, the optimal description of orbital magnetism in complex open-shell systems, such as transition metals, remains an unsolved problem.

5. Conclusions

This work completes the ab initio investigations of orbital magnetic moments and magnetic anisotropy of small clusters of the metals of the Pd group. Our results provide new insights into the correlation between the symmetry and the magnetic properties of the clusters. For clusters with a symmetry axis of order n ⩾ 3, ferromagnetic order is compatible with rotational symmetry if the magnetization direction is parallel to the symmetry axis, but not for perpendicular magnetization. In this case magnetism breaks the crystallographic symmetry of the cluster. For clusters with higher (tetrahedral or octahedral
symmetry) no magnetic subgroup is compatible with a ferromagnetic state. In this case the crystallographic symmetry is broken irrespective of the direction of magnetization. The former case is realized for the dimer, trimer and pentamer, the latter for the tetramer and hexamer (but note that the symmetry can also be broken even in the absence of SOC by a Jahn–Teller mechanism). A novel result of our investigations is that even for a 3d metal such as Ni, the change in the magnetic symmetry leads to small geometric distortions of the cluster such that there is a contribution to the MAE from the elastic energy. However, in this case SOC is not strong enough to affect the energetic ordering between different magnetic isomers. For the 4d metal Pd these effects are more pronounced, but qualitatively similar as for Ni. For a 5d metal such as Pt, SOC is strong enough to stabilize for the smallest clusters structures, which are only metastable in the scalar-relativistic limit. In this case, due to the strong SOC, the magnetic anisotropy energies can be comparable or even larger than the energy differences between different magnetic isomers. Spin moments are isotropic only for Ni clusters, orbital anisotropies defined relative to the magnetic GS can have either sign. Hence, a perturbation treatment postulating that the cluster geometry is frozen, the spin moments are isotropic, and that the MAE is proportional to the orbital anisotropy is not justified for these small clusters.

Acknowledgment

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