

EXCHANGE INTERACTIONS AND MAGNETIC ANISOTROPY IN THE “Ni₄” MAGNETIC MOLECULE

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Abstract

Magnetic properties of a tetrahedral “Ni₄” molecule are discussed in terms of the Heisenberg model, with magnetic anisotropy terms included, and on the basis of first-principle calculations within the density functional theory. It is shown that the isotropic Heisenberg model does not provide an adequate description of magnetization at low temperatures; an inclusion of single-site anisotropy terms does not help to improve the situation either. We suppose that the magnetostriction of the molecule and hence the dependence of interatomic coupling parameters on the magnetization might be important for an adequate description of magnetic properties. The first-principle calculations confirm the system’s general preference for antiferromagnetic coupling, as well as the failure of the isotropic Heisenberg model. A conjugated-gradient search for the relaxed structure of the “Ni₄” molecule in ferromagnetic and antiferromagnetic configurations did not show any clear tendency to diversification of interatomic distances. These calculations however have not yet included the spin-orbit coupling, which can be essential for analyzing the effects of magnetostriction.

Keywords: Molecular magnets; Heisenberg model; Density functional theory, Exchange interactions

1. INTRODUCTION

The system of our present interest belongs to a large family of molecular magnets – metallo-organic or -anorganic substances in which well defined molecular

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fragments possess intrinsic magnetic structure, and can crystallize forming a stable solid phase. An introduction into the subject can be found in the books by Kahn (1993), or Linert and Verdaguer (2003).¹ The practical interest for molecular magnets is heated by high net spin moments and/or large magnetic anisotropy in some of them, that seems promising for dense magnetic storage. Moreover, unique and novel properties of molecular magnets, like quantum tunneling of magnetization (Friedman *et al.*, 1996; Wernsdorfer *et al.*, 1999), open perspectives of basically new applications – manipulation of magnetic states by light, work media for quantum computers, etc.

In the actual stage of “extensive” exploration of the field, as clear guidelines relating chemical composition to properties are still missing, one witnesses a permanent quest on the side of chemists to synthesize new systems with unusual or otherwise so far unknown combination of metal or organic building blocks. “Ni₄” is such a system, where the magnetic coupling between four Ni ions (each carrying spin $s=1$) occurs via a long and chemically not very common path.

In the present contribution, we outline the analysis of known magnetic properties in terms of the Heisenberg model in its simplest form and also with some extensions. Simultaneously, we perform first-principles simulations of the electronic structure and try to estimate magnetic interaction parameters from them.

2. STRUCTURE AND BASIC MAGNETIC PROPERTIES

The full chemical formula of “Ni₄” is $[\text{Mo}_{12}\text{O}_{30}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Ni}(\text{H}_2\text{O})_3\}_4] \cdot 14 \text{H}_2\text{O}$; its synthesis and characterization have been reported by Müller *et al.* (2000). The basic structural unit is a slightly distorted Ni₄ tetrahedron, whose vertices cap the hexagonal faces of the O-bridged Mo₁₂ cage. The crystal structure contains two such units, related by the 180° rotation around an edge of the tetrahedron, as is shown in Fig. 1. The nearest neighbourhood of each Ni atom is (nearly) octahedral O₆, with three apical oxygens saturated by bonded hydrogen, and three others participating in the bonding to Mo atoms. The magnetic interaction path is therefore Ni–O–Mo₂–O–Ni, with the length of 6.6–6.7 Å. The nominal Ni^{II} state corresponds to the $3d^8$ configuration and hence $s=1$. The ground state was found to have the total spin $S=0$ (Schnack *et al.*, 2004).

The quantitative description of magnetic properties (magnetization and magnetic susceptibility) reported by Müller *et al.* (2000) requires to choose an underlying physical model. The traditional simplest choice is that of the Heisenberg model,

¹In a broader perspective, one includes sometimes purely organic magnetic substances, on one side, and three-dimensional connected metalloorganic systems, on the other side, in the definition of molecular magnets.

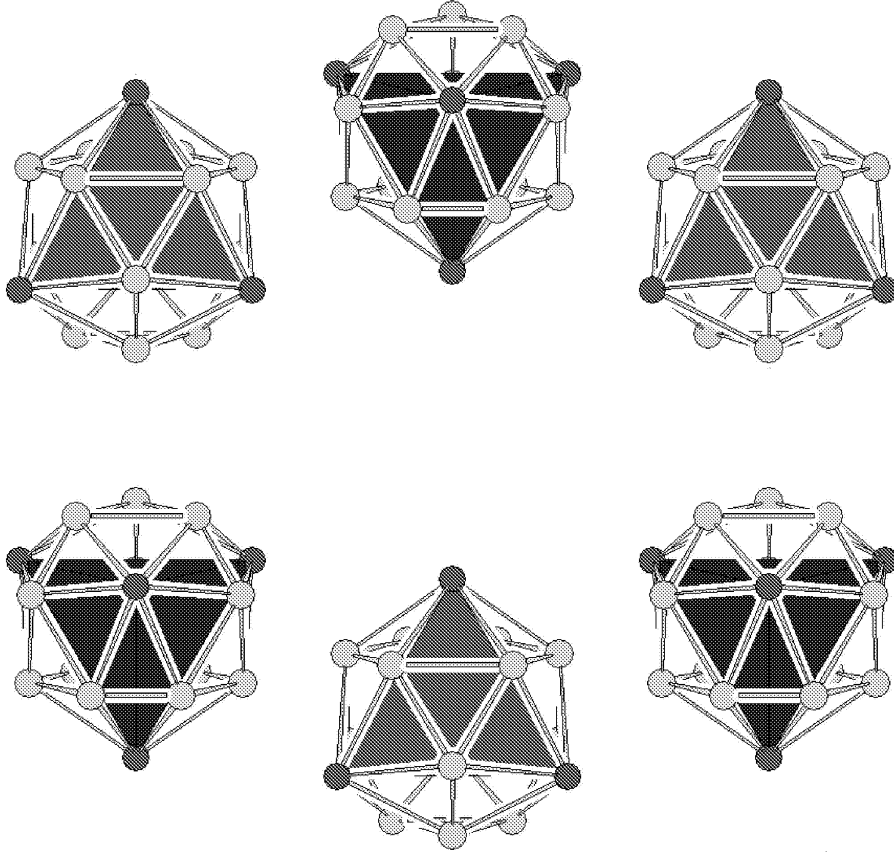


Figure 1: The arrangement of basic structural units $\text{Ni}_4\text{Mo}_{12}$ units in the molecular crystal (courtesy of Paul Kögeler). A slightly distorted Ni_4 tetrahedron (dark circles) is kept together by O-bridged Mo_{12} cage (gray circles).

which we introduce (including the Zeeman term) as follows:

$$\mathcal{H} = J \sum_{\substack{\{\alpha,\beta\} \\ \text{pairs}}}^6 \mathbf{s}_\alpha \cdot \mathbf{s}_\beta + g\mu_B \sum_{\alpha}^4 \mathbf{B} \cdot \mathbf{s}_\alpha. \quad (1)$$

All $s_\alpha=1$, and $J > 0$ corresponds to antiferromagnetic (AFM) coupling in this formulation. In the following, we would need to extend this model over anisotropic effects. The simplest case is an inclusion of the single-ion anisotropy,

$$\mathcal{H} = J \sum_{\substack{\{\alpha,\beta\} \\ \text{pairs}}}^6 \mathbf{s}_\alpha \cdot \mathbf{s}_\beta + D \left[\sum_{\alpha}^4 (\mathbf{e}_\alpha \cdot \mathbf{s}_\alpha)^2 - \frac{8}{3} \right] + g\mu_B \sum_{\alpha}^4 \mathbf{B} \cdot \mathbf{s}_\alpha. \quad (2)$$

with D being the constant of zero-field splitting, and \vec{e}_α the local anisotropy axis for each ion.

With $N=4$ coupled spins $s=1$, the total dimension of problem is

$$(2s + 1)^N = 81 = \sum_{S=0}^4 \sum_{M_S=-S}^S G_S, \quad (3)$$

where $G_{S=0,1,2,3,4} = 3, 6, 6, 3, 1$ are degeneracies of the $|S, M_S\rangle$ states. The exact diagonalisation of this model can be straightforwardly done for any choice of parameter values. The magnetic susceptibility χ and magnetization M are obtained in terms of the partition function Z :

$$Z = \sum_{S=0}^4 \sum_{M=-S}^S G_S e^{-\frac{E_{S,M_S}}{k_B T}}; \quad (4)$$

$$M = -\frac{g\mu_B}{Z} \text{Tr} \left[e^{-\frac{\mathcal{H}}{k_B T}} S_Z \right], \quad (5)$$

$$\chi = \frac{\partial M}{\partial B} = \frac{(g\mu_B)^2}{k_B T Z} \text{Tr} \left[e^{-\frac{\mathcal{H}}{k_B T}} S_Z^2 \right] - \frac{M^2}{k_B T}. \quad (6)$$

Fig. 2 shows the fit of the measured magnetic susceptibility data, as obtained by Paul Kögerler on powder samples and reported by Müller *et al.* (2000), to the isotropic Heisenberg model of Eq. (1). The Heisenberg model yields the Curie–Weiss behaviour,

$$\chi_{\text{CW}} = \frac{C}{T + T_C} \quad \text{with} \quad C = \frac{8(g\mu_B)^2}{3k_B} \quad \text{and} \quad T_C = \frac{2J}{k_B}, \quad (7)$$

from fitting to which one can estimate the values of J and g . Fig. 2 shows that both direct and inverse susceptibility can be satisfactorily fitted through wide temperature range with only slightly varying parameter values, either $\{J=6.6 \text{ K}; g=2.22\}$, or $\{J=8.5 \text{ K}; g=2.27\}$ (Brüger, 2003).

However, the observed field dependence of the magnetization, measured at sufficiently low temperature (0.44 K), cannot be reasonably described by any of these sets of parameters, nor by any other one, within the isotropic Heisenberg model. As is seen in Fig. 3, the Heisenberg model yields equidistant steps in the magnetization curve, with appropriate temperature smearing. In the experimental curve, on the contrary, the steps are not equidistant (in the field strength), moreover they are much stronger smeared, to the extent that the first step is hardly pronounced.

A number of attempts has been undertaken by Brüger (2003) to achieve a reasonable fit to the measured magnetization curve, varying the values of magnetic coupling parameter J and of the zero-field splitting parameter D , various orientations of the external magnetic field relative to the Ni_4 tetrahedron, averaging over different orientations, etc. A non-equidistant steps in the magnetization, somehow similar to those experimentally observed, can be simulated by allowing an increase of coupling constants J with magnetic field. As the physical mechanisms of interatomic

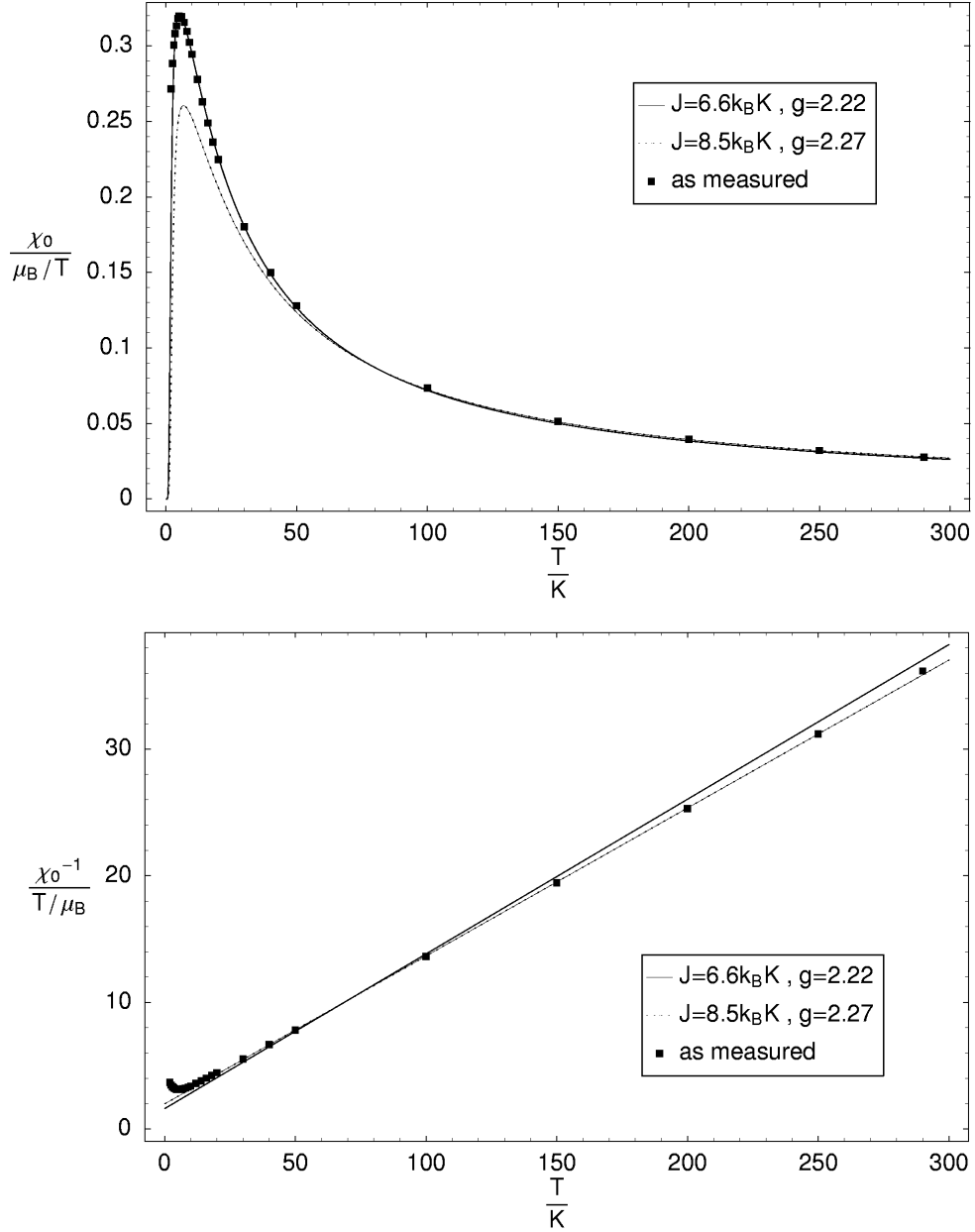


Figure 2: Magnetic susceptibility (top panel) and its inverse (bottom panel), as reported by Müller *et al.* (2000), in comparison to the fit of the Curie–Weiss law with two sets of parameters (Brüger, 2003).

coupling, in the simplest picture, have to do with the overlap of orbitals centered at different sites, a justification of the $J(B)$ dependency might be provided by the variation of interatomic distances in the magnetic field, i.e., the magnetostriction effects. The exponential dependence of interatomic overlap integrals with distance would justify the parametrization $J(B) \sim \exp(B/\gamma)$.

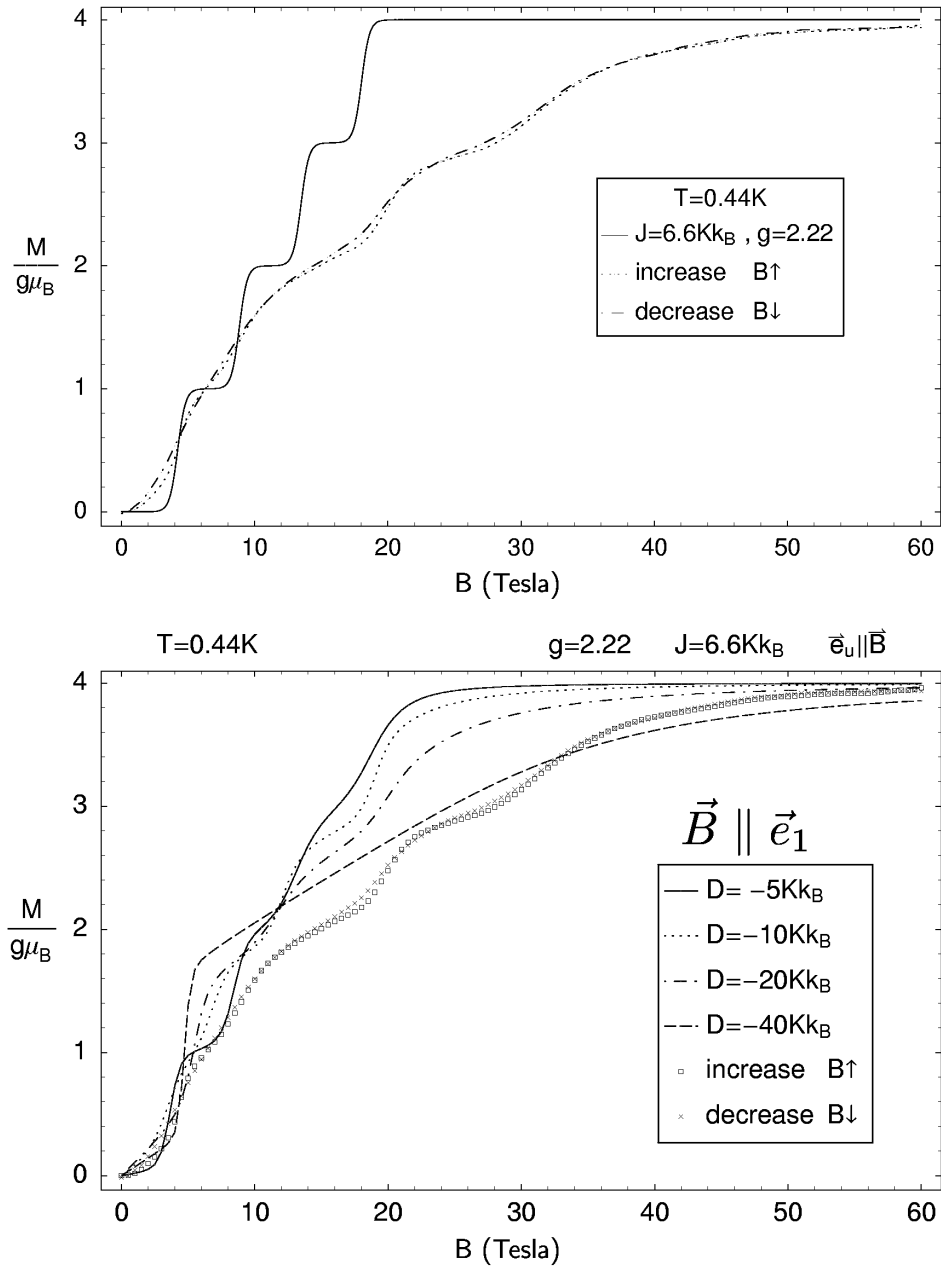


Figure 3: An attempted fit (Brüger, 2003) to the measured (by Müller *et al.*, 2000) magnetization as function of the external magnetic field: within the isotropic Heisenberg model (top panel) and allowing different values of the zero-field splitting parameter D (bottom panel).

Fig. 4 shows a fit to the experimental magnetization and magnetic susceptibility with a zero-field splitting constant included in the Heisenberg model *and* an empirical magnetic field dependency of the magnetic interaction parameter J . The exact diagonalisation of the corresponding model Hamiltonian yields an almost acceptable

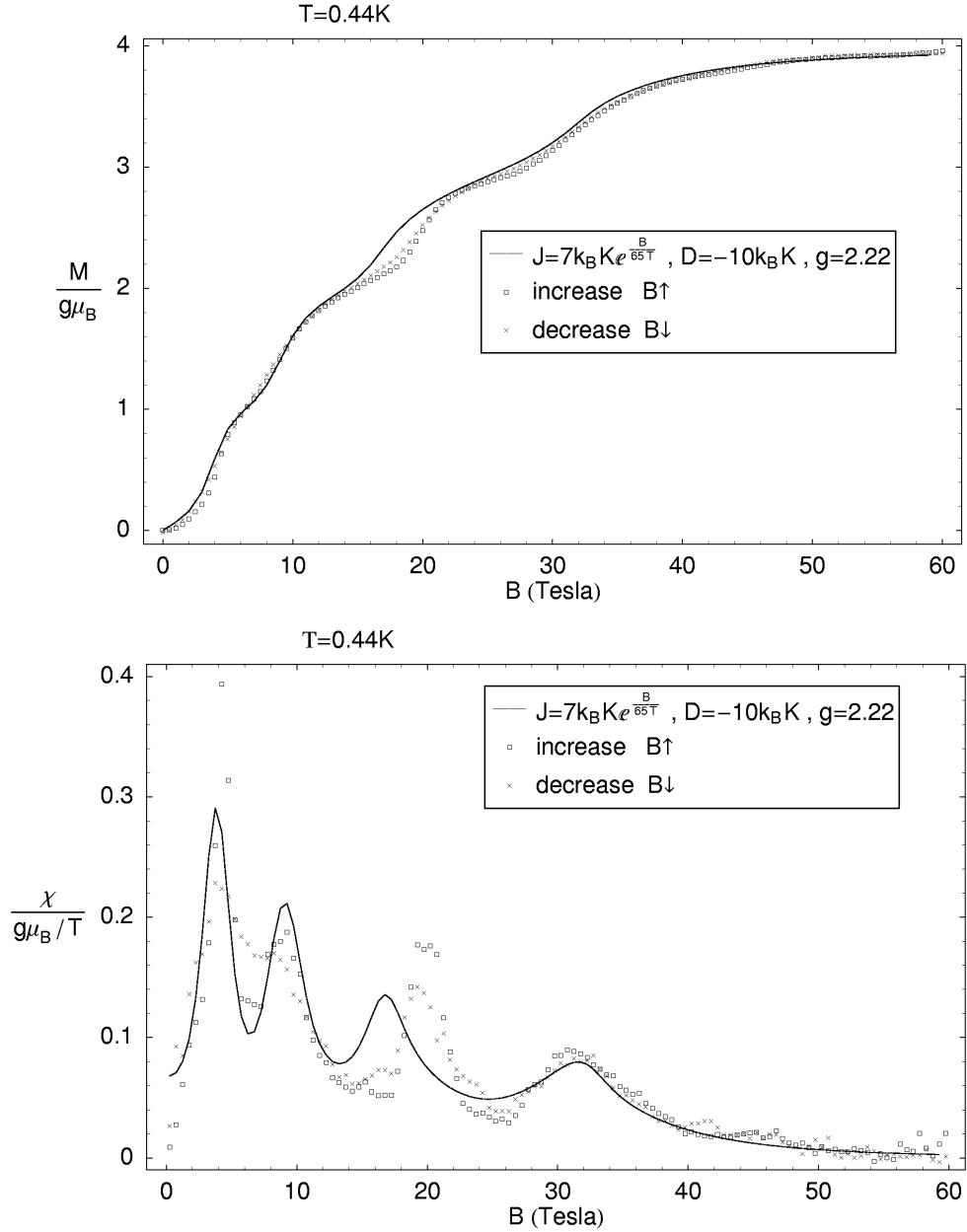


Figure 4: A fit to the measured (by Müller *et al.*, 2000) magnetization as function of the external magnetic field B , according to the Heisenberg model with zero-field splitting D , averaged over 1000 randomly generated orientations, in combination with B -dependent magnetic coupling (top panel); the corresponding magnetic susceptibility (bottom panel).

description of the experimental trends, yet leaves the questions open about the microscopic origins, and the specific form, of the model parameters' variation with magnetic field.

3. DFT CALCULATIONS SETUP

The first-principles approach, on the contrary, is able to compare the energies of different magnetic configurations without making assumptions about relevant physical interactions in the system. Moreover, the values of model Hamiltonian parameters, like exchange couplings J and anisotropy constants D , can be in principle evaluated without referring to any experimental data. An abundant literature exists notably to the subject of J (see, e.g., Calzado *et al.*, 2002a,b, for a recent discussion on the subject). We emphasize the difference between multi-configurational quantum-chemical approach, and that of the density functional theory (DFT). The former refers to the differences in energy of, e.g., singlet and triplet multi-determinantal states. In the DFT, such properties are not accessible, but one can compare the expectation values of the Hamiltonian in specially prepared states, e.g., a triplet (ferromagnetic) and the broken-symmetry (antiferromagnetic) ones. For the comparison of approaches and a more detailed discussion, see Postnikov *et al.* (2004b). Further reference magnetic configurations can be created in the DFT by using the fixed spin moment (FSM) scheme (Schwarz and Mohn, 1984). The discussion on the applicability of the Heisenberg model based on the results of DFT calculations and comparison of the FSM results for another molecular magnet, hexanuclear “ferric wheel”, has been given in Postnikov *et al.* (2004a). In the following, we make a similar analysis for the “Ni₄” system. As in the last cited paper, the DFT calculations have been done with the SIESTA method (Soler *et al.*, 2002), using norm-conserving pseudopotentials (Troullier and Martins, 1991) and a compact basis set of strictly localized numerical functions. Specifically, we used a triple- ζ basis for Mo $4d$ and Ni $3d$ states, double- ζ with polarization orbitals for O $2s$ and $2p$, H $1s$, Mo $4p$, Ni $4p$, and single- ζ with polarization orbitals for Mo $5s$ and Ni $5p$. The energy shift parameter, governing the spatial confinement of basis function, was 20 mRy. The exchange-correlation was treated in the generalized gradient approximation after Perdew *et al.* (1996). A molecular fragment with 104 atoms, in total, was treated as an isolated molecule in a cubic simulation box with the edge size 20 Å. The cutoff parameter defining the real-space mesh for solving the Poisson equation was set to 200 Ry, that resulted in a $180 \times 180 \times 180$ grid in the abovementioned cubic simulation cell. In order to smoothen the variations of the total energy and other properties due to the “eggbox effect”, an averaging of calculated grid-dependent properties over a finer fcc-type sub-grid has been done, as described by Soler *et al.* (2002). The calculations have been done for the “as determined” crystal structure, i.e., corresponding to the ground state of $S=0$. We allowed moreover a structure relaxation for antiferromagnetic (AFM, $S=0$) and ferromagnetic (FM, $S=1$) configurations.

Before discussing the results it should be noted that the SIESTA method does not include the treatment of spin-orbit interaction, hence it is not possible to discuss the magnetic anisotropy parameters on the basis of calculation. In principle, the calculation of zero-field splitting D is not only possible, but yields the quantitative results of very high accuracy. Pederson and Khanna (1999a,b) proposed a method for calculation of the second-order anisotropy energies, which yielded perfect agree-

ment with experiment for the Mn_{12} -acetate (see the cited works) and for a number of other molecular magnets (see Table 3 in Postnikov *et al.*, 2004b).

4. FIXED SPIN MOMENT CALCULATIONS

The FSM scheme fixes the total number of electrons in majority- and minority-spin channels. This amounts to imposing an effective external magnetic field, which – at least in metal systems – introduces a difference in the chemical potential for majority- and minority-spin electrons. When applied to molecular magnets, the fixed total moment can be only an integer (and usually even) amount of Bohr magnetons. Isolated magnetic molecules have discrete Kohn-Sham energy levels, and normally, a non-zero HOMO-LUMO gap. Therefore both spin channels may still possess a common chemical potential (if their respective HOMO-LUMO gaps do overlap), or they may need, similarly to the case of a metallic system, an external magnetic field for enforcing the splitting. In the former case, the DFT solutions corresponding to different FSM values coexist as metastable states, whose total energies can be directly compared. In the latter case, a Zeeman term must be taken into account as an additional energy needed to split the chemical potentials in two spin channels. These are the foundations of our FSM analysis for Ni_4 .

Fig. 5 shows the total energies for a number of configurations with different FSM values (left panel), along with corresponding HOMO-LUMO gaps in two spin channels. For setting up an AFM configuration (zero FSM value), the local magnetic moments of two (arbitrary, due to nearly perfect tetrahedral symmetry) Ni atoms were inverted. This configuration then always survived in the course of self-consistent calculation. The corresponding spin-resolved local densities of states (DOS) for two oppositely magnetized Ni atoms and several of their neighbours are shown in Fig. 6. A fragment of the molecule, including the path between two Ni atoms, is depicted in the inset. It is well seen that the local DOS at the Ni site in the majority-spin channel is dominated by a fully occupied $3d$ subband, which forms a single narrow peak. In the minority-spin channel, one sees a crystal-field splitting into the t_{2g} (occupied) and the e_g (empty) energy levels. Such clear separation, without a pronounced further splitting, is due to the fact that the oxygen octahedra around the Ni atoms are almost undistorted. The above electronic configuration corresponds to the spin value $s=1$ per Ni atom, consistently with experiment. The value of the *local* magnetic moment per Ni atom, as determined by the Mulliken population analysis, may however differ from $2 \mu_B$, depending on the spatial distribution of the spin density and its decomposition into different basis orbitals. In particular, the charge transfer from Ni to O reduces the nominal value of the majority-spin $\text{Ni}3d$ occupation, at the same time inducing magnetic moments at the oxygen ligands. The values of local magnetic moments at several representative atoms is shown in Fig. 6 on the left to each plot. Obviously the Ni atom with its six O neighbours makes a fragment which essentially carries the magnetic moment of $2 \mu_B$; the magnetization of Mo atoms is not pronounced.

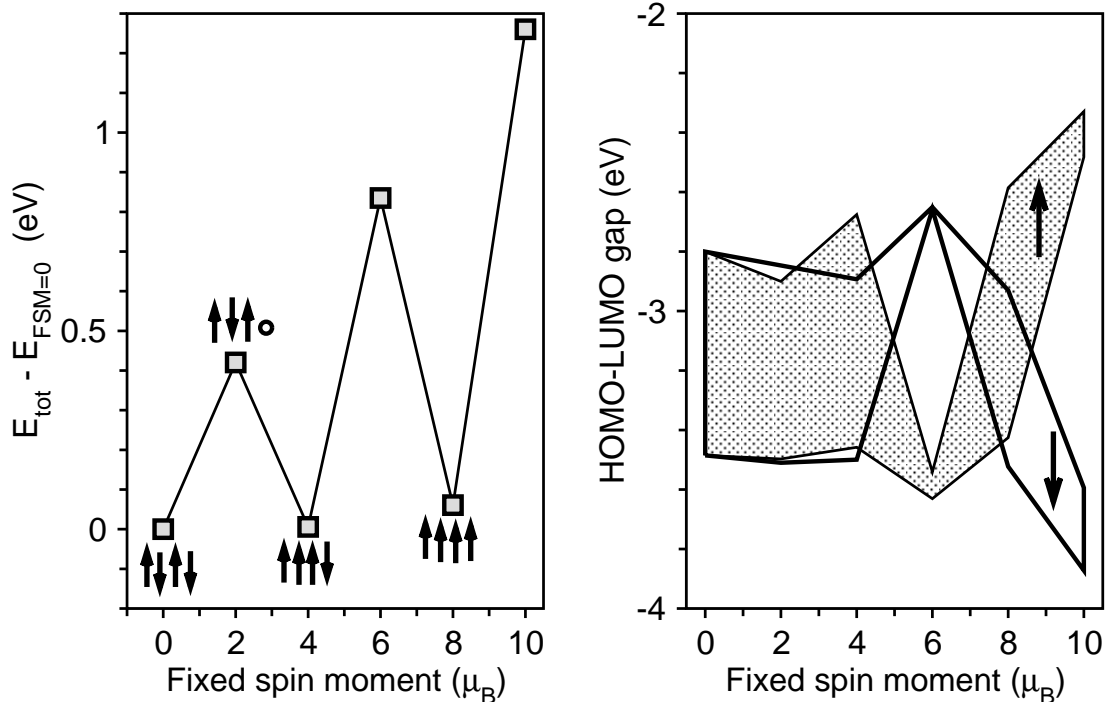


Figure 5: Total energy relative to that of the AFM ground state (left panel) and HOMO-LUMO gap values in two spin channels (right panel) from the FSM calculations. The relative orientation of magnetic moments associated with Ni atoms (nominally $s=1$) is shown schematically in the left panel for different magnetic configurations.

Such cumulative spins $s=1$ per NiO_6 fragment remain relatively intact if one imposes different values of the fixed spin moment. The AFM state ($\text{FSM} = 0 \mu_B$), the one with the spin of one NiO_6 group inverted ($\text{FSM} = 4 \mu_B$) and the FM state ($\text{FSM} = 8 \mu_B$) can all easily be realized, and differ only slightly in their total energies. It is noteworthy that the imposed FSM value of $2 \mu_B$ converges to a configuration where three NiO_6 groups maintain the spins $s=1$, and the fourth Ni atom becomes non-magnetic (see Fig. 5, left panel). This configuration lies higher in energy than the three previously mentioned ones. Yet in all four cases there is a common gap between occupied and unoccupied states in both spin channels (see Fig. 5, right panel), that means that all four configurations can be realized as metastable magnetic solutions, without imposing an external magnetic field and hence without an extra energy cost due to the Zeeman term.

The energy of the $\text{FSM} = 2 \mu_B$ configuration cannot be used for the mapping of calculation results to the Heisenberg model, because it contains a different number of isolated spins as the other three cases. For $\text{FSM} = 0, 4,$ and $8 \mu_B$ the difference in energies comes from different orientation of “rigid” magnetic moments, and hence can serve for an attempt to extract the magnetic interaction parameters. As can be seen in Table I, which compares the energy differences between three orientations of four $s=1$ spins according to the Heisenberg model and to the calculation

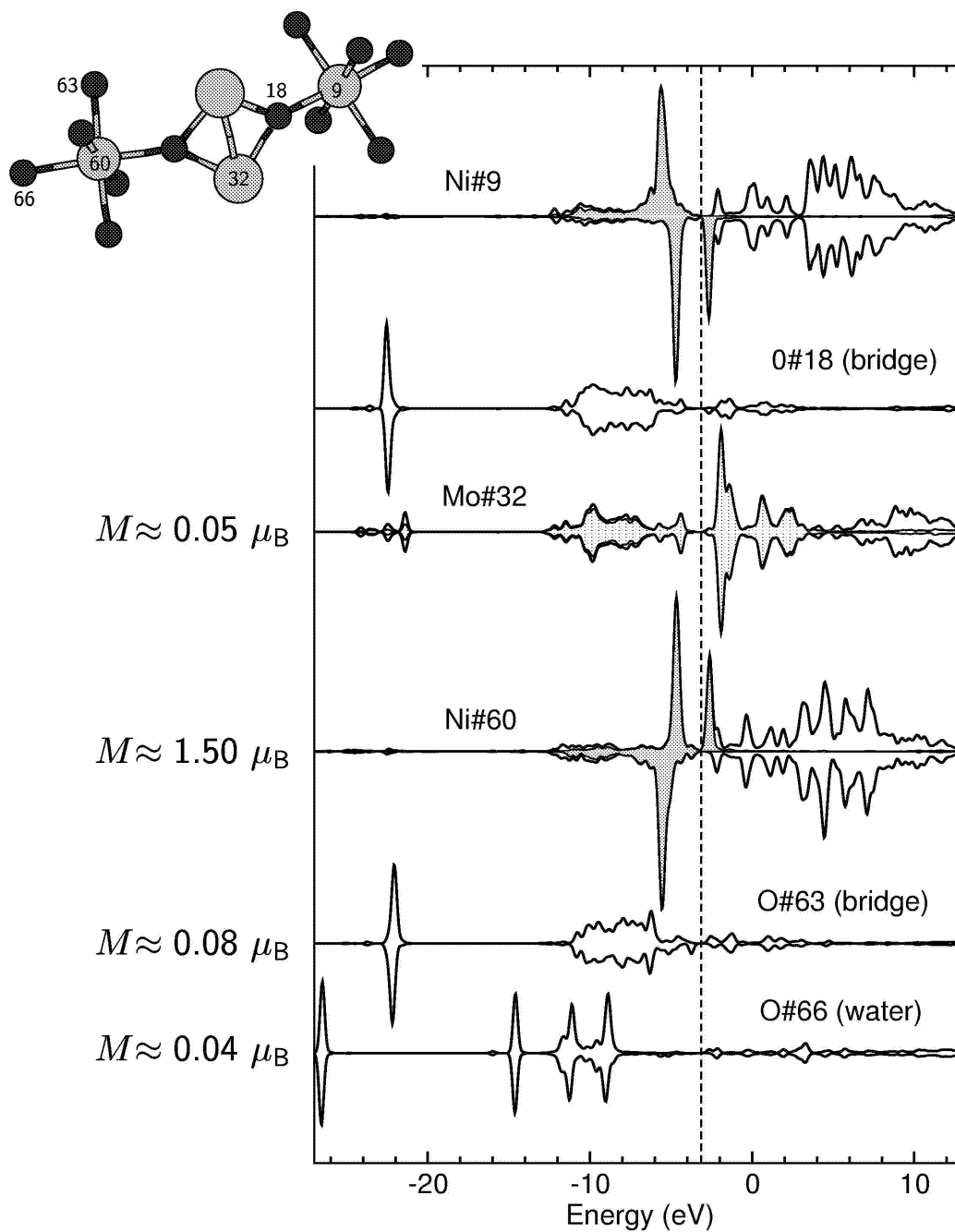


Figure 6: Local spin-resolved DOS of two Ni atoms in AFM configuration along with bridging O and Mo atoms. The inset shows the corresponding part of the “Ni₄” molecule with the numbering of atoms. Local magnetic moments according to Mulliken population analysis are indicated on the left. The shaded areas for Ni (Mo) atoms show the contributions of the 3d (4d) states.

Table 1: An attempted mapping of the calculated total energies for three metastable FSM solutions onto the Heisenberg model. The relations between total energy values are not compatible with the predictions of the model. Order-of-magnitude estimates of the J parameter from two energy differences to the ground state are 87 K and 35 K.

FSM (μ_B)	$\sum_{\{i,j\}\text{pairs}} J \mathbf{s}_i \mathbf{s}_j$	$E_{\text{tot}} - E_{\text{tot}}^{(\text{FSM}=0)}$ (meV)
0	$-2J$	0
4	0	6
8	$6J$	60

results, such extraction is not straightforward. Actually it is an indication that the Heisenberg model does not reasonably describe magnetic interactions in the “Ni₄” molecule. This qualitative observation is consistent with the analysis of experimental data discussed above. The best one can do is to provide an order-of-magnitude estimate of the Heisenberg exchange parameter, which is positive, i.e. favouring the antiferromagnetic coupling (in the definition of Eq. 1), and hence consistent with experiment, and has the magnitude $J \approx 35\text{--}87$ K. The earlier discussed J value estimated from the fit to experimental results of magnetic susceptibility (Fig. 2) are 6–9 K. To some extent, the difference can be due to underestimating the intraatomic correlation effects in a conventional DFT calculation. It has been shown by Boukhvalov *et al.* (2002) for the Mn₁₂-acetate molecule and by Boukhvalov *et al.* (2003) for the “V₁₅” molecular magnet that an artificial enhancement of the on-site Hubbard-like correlation within the LDA+ U formalism (Anisimov *et al.*, 1997) favours the localization of the magnetic moment at the $3d$ atoms and tends to reduce the interatomic magnetic interactions. However, the selection of “correlated” states has to be done *ad hoc* in the LDA+ U formalism, and the magnitude of the necessary correction enters the calculation as an external tuning parameter.

It should be noted that the AFM configuration, being a broken-symmetry state, is *not* a faithful representation of the true $S=0$ ground state of the system. Moreover it is obviously a frustrated state, because each Ni atom interacts with one Ni magnetized in parallel and two antiparallely magnetized counterparts, whereas all coupling constants are expected to be identical, for symmetry reasons. Nevertheless, the calculated total energy of this broken symmetry state (Table I) may be mapped onto the predictions of the Heisenberg model, taken together with the results for other two lowest-energy configurations, according to the FSM analysis of Fig. 5.

5. STRUCTURE RELAXATION

In conclusion we discuss the structure optimization of the “Ni₄” molecule in AFM and FM configurations, which correspond to the FSM values of 0 and 8 μ_B , cor-

respondingly. The aim of the simulation was to check whether the interatomic distances in the molecule would tend to become pronouncedly different in two magnetic configurations, that would probe the assumption of large magnetostriction in the molecule. Our preliminary results (Fig. 7) does not seem to confirm the latter hypothesis, but definite conclusion can be only be made on the basis of fully relativistic calculations. Our present simulation includes relativistic effects but the spin-orbit interaction; consequently, the influence of magnetic structure on total energy and forces is only via the hybridisation which is slightly different in FM and AFM configurations. When starting from the reported experimental geometry,

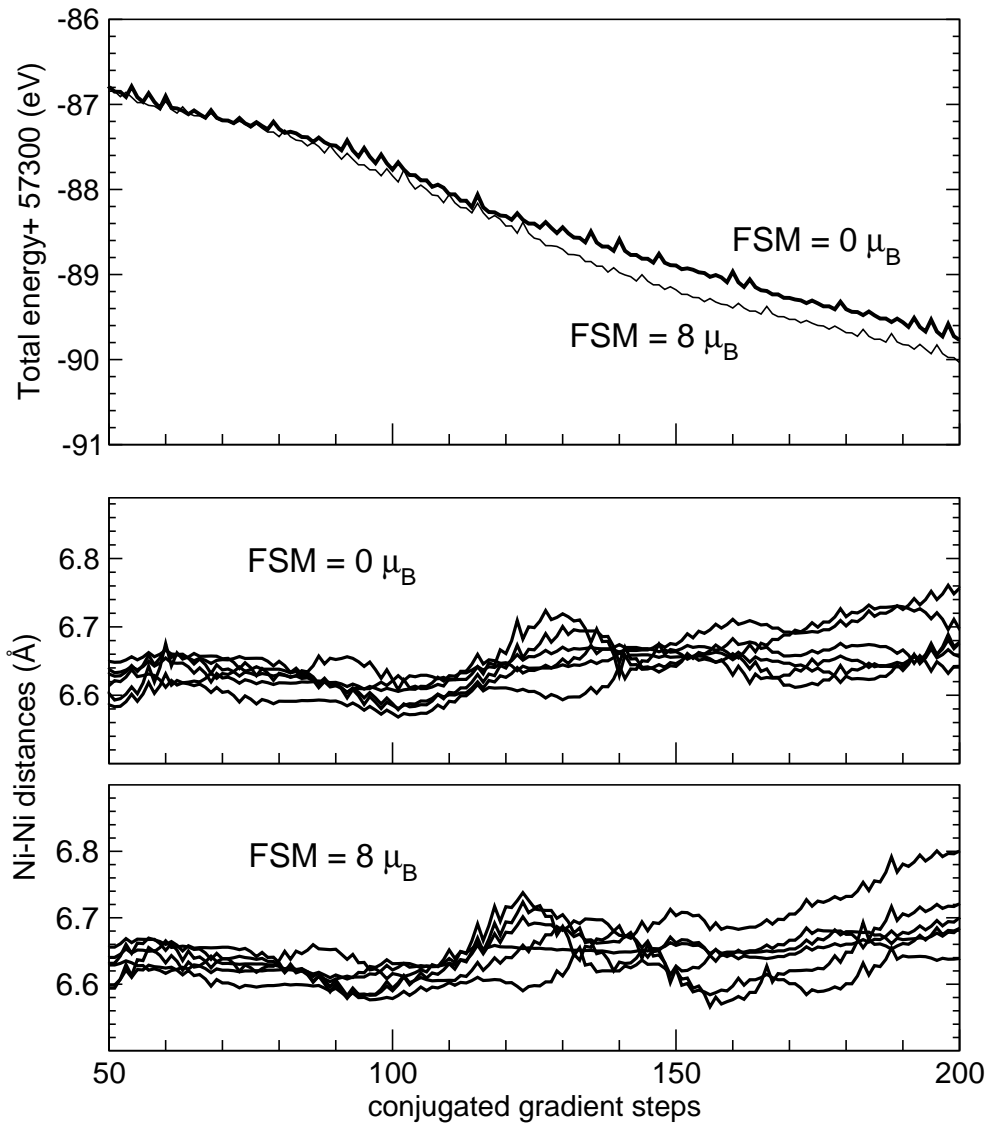


Figure 7: Total energy (top panel) and six Ni–Ni distances (two bottom panels) in the course of unconstrained structure optimization, for FSM values $0 \mu_{\text{B}}$ (AFM state) and $8 \mu_{\text{B}}$ (FM state).

an initial stage of relaxation (not shown in Fig. 7) substantially lowered the total energy, and induced strong fluctuations of interatomic distances. Eventually the molecule recovers Ni–Ni distances of 6.6–6.7 Å, not pronouncedly different in FM and AFM cases. A subsequent smooth lowering of the total energy does not yet seem converged after 200 conjugated gradient steps.

The fact that the total energy of the FM configuration in Fig. 7 lies, over a large number of simulation steps, lower than that of the AFM, does not contest our above result concerning the system’s tendency for the AFM coupling. The two curves in the upper panel of Fig. 7 reflect two different relaxation histories, so that two solutions which accidentally correspond to the same step number stay in no obvious relation to each other. A meaningful comparison of the FM and AFM total energies requires either the identical structure (as it has been done in the previous section), or full relaxation of structures in two magnetic configurations to be compared.

Summarizing, we attempted a fit of experimental magnetic susceptibility and magnetization data for the “Ni₄” magnetic molecule to the Heisenberg model, including zero-field splitting (single-ion anisotropy) and allowing variations of exchange parameters J with the external magnetic field. It seems that fixed (magnetic field and temperature-independent) values of J do not allow to achieve an acceptable fit of experimental dependencies. As a microscopic reason for the J dependency on magnetic field, we assume a magnetostriction in the “Ni₄” molecule to play an important role. Without the deformation of the molecule in the magnetic field taken into account, the results of first-principles calculations are consistent with experimental data: they indicate an antiferromagnetic interaction between Ni atoms, and confirm the conclusion that the magnetic properties of the system cannot be fit to the isotropic Heisenberg model. An attempt to simulate the relaxation of the molecule from first principles indicated a not very pronounced difference in the Ni–Ni distances between ferromagnetic and antiferromagnetic configurations of the molecule. However, the spin-orbit interaction has not been included in the present simulation; yet it is essential for a precise treatment of magnetic anisotropy and magnetostriction, so its inclusion is likely to affect the results.

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