

## Magnetic Anisotropy of 3d Transition-Metal Clusters

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The magnetic anisotropy energy (MAE) of 3d transition-metal clusters was determined by calculating *self-consistently* the effects of the spin-orbit coupling on the spin-polarized charge distribution and on the electronic spectrum for different orientations of the magnetization. The MAE shows a complicated, nonperturbative behavior as a function of cluster size, structure, bond length, and *d*-band filling. In agreement with experiment, the MAE of small clusters is found to be considerably larger than in the corresponding crystals, often even larger than in thin films. Remarkably, the in-plane anisotropy can be of the same order of magnitude as the off-plane anisotropy.

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The magnetic anisotropy is one of the main characteristics of a magnetic material. It determines the low-temperature orientation of the magnetization with respect to the structure of the system and the stability of the magnetization direction in the case of single-domain particles. These are properties of crucial importance in technological applications (e.g., magnetic recording or memory devices) where the magnetization must be pinned to a given direction in space. In past years the main research activity in this field has been the study of low-dimensional systems which present novel magnetoanisotropic properties as a result of their reduced dimensionality and symmetry. In this context, the magnetic anisotropy of small 3d transition-metal (TM) clusters deserves special attention, not only from a purely theoretical point of view but also because of its implications in cluster-beam Stern-Gerlach experiments [1,2]. Indeed, the magnetic anisotropy and the resulting coupling of the magnetization to rotations and internal vibrations provide a natural mechanism for describing the phenomenon of spin relaxation within *isolated* clusters in an external magnetic field, first observed in Fe<sub>N</sub> by de Heer and co-workers [1,2]. Furthermore, the magnetic anisotropy energy (MAE)—i.e., the energy involved in rotating the magnetization from a low-energy direction (easy axis) to a high-energy direction (hard axis)—is one of the key parameters characterizing the dynamics of rotating clusters in a Stern-Gerlach magnet. It determines the blocking temperature above which a superparamagnetic behavior holds and may lead to a resonancelike coupling between the rotational frequency and the Zeeman splittings [1–6]. From these investigations—as well as from Mössbauer studies on supported Fe nanoparticles [7]—it was also inferred that the MAE of TM clusters is considerably larger than in the corresponding crystals. Now, in spite of this remarkable research activity, and although the potential importance of the magnetic anisotropy was recognized from the very beginning, the subject has, so far,

never been investigated from an electronic point of view. It is the goal of this Letter to present the first self-consistent determination of the magnetic anisotropy of small TM clusters and to reveal how the MAE depends on relevant external variables such as cluster size, structure, bond length, and *d*-band filling.

Previous studies of the magnetic properties of TM clusters [8,9] have evidenced the crucial role played in these systems by the redistributions of the spin-polarized electronic density between atoms having different local environments. These spin-density transfers, which, in particular, are responsible of the enhancement of the magnetic moments, are essential for the determination of the cluster electronic structure. Given the fact that the effects of the spin-orbit (SO) interactions are very sensitive to the details of the electronic spectrum, one may readily expect that the MAE will depend sensitively on the spin and charge distribution and on the variables that define it (e.g., the size and the structure of the system or the number of *d* electrons per atom). For this reason, and in order to include also the contributions to the magnetic anisotropy resulting from eventual density redistributions *induced* by the SO coupling, it is our aim to perform accurate self-consistent calculations for each of the considered orientations of the magnetization and to obtain the MAE in a nonperturbative fashion as the difference between electronic energies. Consequently, we extend the self-consistent tight-binding approach proposed in Ref. [9] by including the SO interactions, which give the dominant contribution to the MAE of small clusters and ultrathin films [10]. The electronic Hamiltonian is then given by the sum of three terms. Besides the interatomic hopping term  $H_0$  and the Coulomb interaction term  $H_C$  treated in the unrestricted Hartree-Fock approximation—which are the same as in Ref. [9]—the SO coupling term

$$H_{SO} = -\xi \sum_{i,\alpha\sigma,\beta\sigma'} (\vec{L}_i \cdot \vec{S}_i)_{\alpha\sigma,\beta\sigma'} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{i\beta\sigma'} \quad (1)$$

is now taken into account.  $(\vec{L}_i \cdot \vec{S}_i)_{\alpha\sigma,\beta\sigma'}$  refer to the intra-atomic matrix elements of  $\vec{L} \cdot \vec{S}$  between the orbitals  $\alpha, \beta$  of spin  $\sigma, \sigma'$  at atom  $i$ , which couple the up and down spin manifolds and which depend on the relative orientation between the average magnetization  $\langle \vec{S} \rangle$  and the cluster structure. For each orientation of the magnetization the local densities of electronic states (DOS)  $\rho_{i\alpha\sigma}(\varepsilon)$  are determined self-consistently, thus including the coupled contributions of  $H_0$ ,  $H_C$ , and  $H_{SO}$  on the same footing.

The electronic energy per atom  $E_\delta$  is calculated from

$$E_\delta = \frac{1}{N} \sum_{i\alpha\sigma} \int_{-\infty}^{\varepsilon_F} \varepsilon \rho_{i\alpha\sigma}(\varepsilon) d\varepsilon - E_{dc}, \quad (2)$$

where  $\delta$  refers to the magnetization direction (e.g.,  $\delta \equiv x, y, z$ ) and  $E_{dc}$  to the double counting correction [9]. The MAE  $\Delta E$  is given by the change in the electronic energy  $E_\delta$  associated with a change in the orientation of the magnetization  $\langle \vec{S} \rangle$  for a fixed position of the atoms. For example,  $\Delta E = E_x - E_z$  measures the relative stability of the magnetization along the  $x$  and  $z$  axes. To our knowledge, this is the first time such a fully self-consistent study of the MAE is performed.

The two-center hopping integrals and the intra-atomic Coulomb integrals used in the calculations correspond to Fe and are taken from Ref. [9]. The corresponding value of the SO coupling constant is  $\xi = 0.05$  eV [10]. Trends for other 3d TM's are inferred by varying the  $d$ -band filling  $n_d$ . The DOS  $\rho_{i\alpha\sigma}(\varepsilon)$  are computed by using Haydock, Heine, and Kelly's recursion method. The number of levels used in the continued fraction expansion of the Green's functions is such that the results for  $\rho_{i\alpha\sigma}(\varepsilon)$  correspond to the exact solution of the single-particle problem. The self-consistent equations for the spin-polarized density distribution are solved with an accuracy  $\epsilon$ , which is high enough to ensure that the small energy differences involved in the MAE are determined reliably (typically  $\epsilon \leq 10^{-9}$  electron/atom). Moreover, the stability and accuracy of the results are always explicitly checked by performing two independent self-consistent calculations choosing different quantization axes of the orbital angular momentum (i.e., with a different tight-binding basis). Within the model, the estimated accuracy of the calculated MAE is  $10^{-5}$  eV.

The magnetization direction can be chosen without restrictions. In particular, we will consider a perpendicular magnetization direction, along the  $z$  axis, as well as one or more in-plane directions, within the  $x$ - $y$  plane. This plane corresponds to the plane of the cluster, in the case of bidimensional structures, or to the plane orthogonal to the principal  $C_n$  symmetry axis (see Fig. 3). In this way we determine both the perpendicular and in-plane MAE's, a particularly interesting issue, since so far the importance of the latter has never been assessed in the framework of an electronic theory.

In Fig. 1 results are given for the MAE  $\Delta E$ , for the orbital angular momentum  $\langle L_\delta \rangle$  along the magnetization

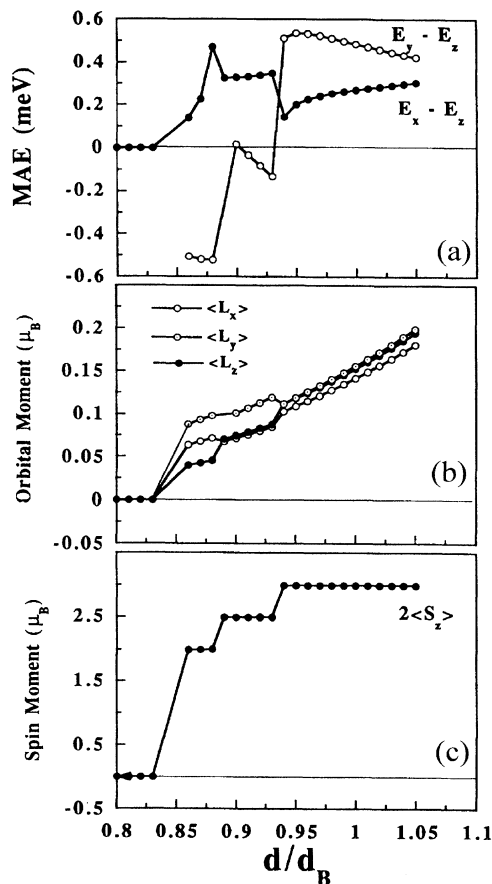


FIG. 1. Magnetic anisotropy energy (MAE), orbital magnetic moment, and spin magnetic moment of  $\text{Fe}_4$  with rhombohedral structure as a function of the bond length  $d$  ( $d_B$  is the bulk nearest-neighbor distance). The considered directions of the magnetization,  $x$ ,  $y$ , and  $z$ , are illustrated in the inset of Fig. 2.

direction  $\delta = x, y, z$ , and for the average perpendicular spin projection  $\langle S_z \rangle$  of  $\text{Fe}_4$  having a rhombohedral structure (see inset, Fig. 2). These results are representative of a much larger number of studied sizes and structures. The MAE is given as a function of the bond length  $d$ , which allows us to determine the role of cluster relaxation and to infer the possible coupling of the magnetization direction to vibrations and distortions. The variations of  $d/d_B$  ( $d_B$  is the bulk bond length) correspond to a uniform relaxation for the given cluster geometry and quantify how  $\Delta E$ ,  $\langle L_\delta \rangle$ , and  $\langle S_z \rangle$  depend on the local environment of the atoms. For all studied clusters the modulus of the spin magnetization  $|\langle \vec{S} \rangle|$  depends very weakly on the direction of the magnetization (e.g.,  $|\langle S_z \rangle - \langle S_x \rangle| \sim 10^{-3} - 10^{-4}$ ). Since the changes in  $|\langle \vec{S} \rangle|$  for the different orientations would be indistinguishable in the scale of the plots, only the results for  $\langle S_z \rangle$  are shown.

From Figs. 1(a) and 1(c) it is clear that the variations of the MAE as a function of  $d/d_B$  are related to the

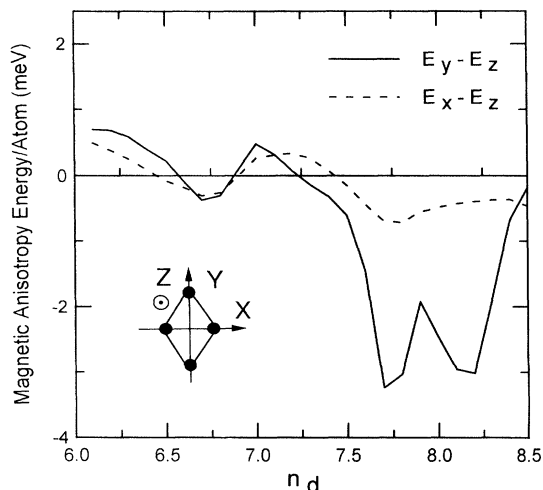


FIG. 2. Magnetic anisotropy energy (MAE) of a rhombohedral four-atom transition-metal cluster as a function of the  $d$ -band filling  $n_d$ . Results are given for the off-plane (full line) and in-plane (dashed line) MAE's. The considered directions of the magnetization,  $x$ ,  $y$ , and  $z$ , are illustrated in the inset.

variations of  $\langle S_z \rangle$  and to the resulting changes in the electronic spectrum. For large values of  $d/d_B$  the spin magnetic moments are saturated:  $\langle S_z \rangle \approx (10 - n_d)/2 = 3/2$  [11]. When  $d/d_B$  decreases, discrete changes in the spin polarization,  $\Delta\langle S_z \rangle$ , occur and nonsaturated spin magnetizations are obtained. As discussed in Ref. [9],  $\Delta\langle S_z \rangle = 2l/N$ , where  $l$  is the number of electrons that flip their spin. For constant values of  $\langle S_z \rangle$ , i.e., for  $d/d_B$  between two spin flips, MAE and  $\langle L_\delta \rangle$  vary continuously, since the electronic spectrum and the local magnetic moments are continuous functions of  $d/d_B$ . This is not the case when a spin flip occurs, since here a strong and discontinuous redistribution of the spin-polarized electronic density takes place. This causes important changes in the energy-level structure around the Fermi energy  $\varepsilon_F$  which modify the details of the SO mixing between these states. The resulting changes in the electronic energy depend, of course, on the explicit form of  $H_{SO}$  and therefore on the direction of the magnetization (see Fig. 1). Consequently, very significant and discontinuous variations of the MAE are observed, which may even lead to a change of sign of the MAE as the spin magnetization  $\langle S_z \rangle$  decreases. The importance of determining the spin-polarized charge distribution *self-consistently* is evident [12].

Under certain assumptions (second-order perturbation in the SO coupling and neglect of interactions between unlike spins)  $\Delta E = E_\delta - E_\gamma$  is approximately proportional to the difference of the projections of the orbital angular momenta  $L_\gamma - L_\delta$  [10]. Our self-consistent calculations show that this relation is not valid in general (see Fig. 1). However, it often works qualitatively well

when the difference in  $L$  is large. Notice, furthermore, that the rhombohedral  $\text{Fe}_4$  cluster presents a remarkable in-plane anisotropy  $E_x - E_y$ , which in the range  $0.83 \leq d/d_B \leq 0.93$  is even larger than the usually considered off-plane anisotropy  $E_z - E_\delta$  ( $\delta = x, y$ ). A similar situation is found for other clusters and band fillings as it will be discussed below. This new result also indicates that the uniaxial anisotropy models [5,6] are not strictly applicable in this case.

The trends for other transition metals and the effects of possible  $sp-d$  charge transfers can be inferred from Fig. 2, where the MAE of a four-atom rhombohedral cluster is given as a function of the  $d$ -band filling  $n_d$ . In the considered range of  $n_d$  the self-consistent calculations yield saturated magnetic moments. For values of  $n_d$  close to that of Fe ( $6.5 \leq n_d \leq 7.5$ ) the MAE is very small ( $\Delta E \sim 0.1$  meV) and the easy direction of the magnetization alternates between the  $x$ - $y$  plane and the  $z$  axis. The situation changes, however, for values close to that of Co ( $7.5 \leq n_d \leq 8.5$ ). Here a remarkably large in-plane anisotropy is found ( $E_x - E_y \approx 2-3$  meV) favoring the orientation of the magnetization along the  $y$  axis. Notice that if only one direction in the  $x$ - $y$  plane would have been considered, e.g., the  $x$  direction, quantitatively wrong conclusions would have been obtained, since the in-plane anisotropy is quite large.

In Table I we present results for the MAE of  $\text{Fe}_4$  clusters—both perpendicular to the  $x$ - $y$  plane  $E_x - E_z$  and within the  $x$ - $y$  plane  $E_x - E_y$ —for the different structures and sizes illustrated in Fig. 3. The strong and apparently irregular behavior of  $\Delta E$  as a function of cluster size  $N$  and bond length  $d$  precludes us from deriving simple general rules. However, we may notice that the MAE is much larger in small clusters than in the corresponding crystalline solids. Moreover,  $\Delta E$  is often even larger than in thin films, for instance, values of  $\Delta E \sim 4-5$  meV are frequent in Table I. These results are in agreement with what is inferred from experiments on free clusters [4,5] and on supported Fe nanoparticles [7]. Furthermore, also note that  $\Delta E$  is much more sensitive to the geometrical structure of the cluster than the magnetic moments [9]. Indeed, changes of sign in  $\Delta E$  are found even in situations where the magnetic moments are saturated and consequently structure independent (for example, for  $N = 6$  and  $d/d_B = 1.05$ ). As discussed before, an important in-plane MAE exists ( $\sim 0.1-1$  meV), which is, of course, larger for low-symmetry structures [for example, for  $N = 5$  (e)] and which decreases, though not monotonically, as the maximum angle between nonequivalent  $x$  and  $y$  directions decreases (see Table I and Fig. 3).

Summarizing, a systematic study of the magnetic anisotropy of small  $3d$  TM clusters has been performed, which has revealed a variety of new interesting behaviors of the MAE as function of cluster size, structure, bond length, and  $d$ -band filling. A significant contribution to the microscopic understanding of the magnetoanisotropic

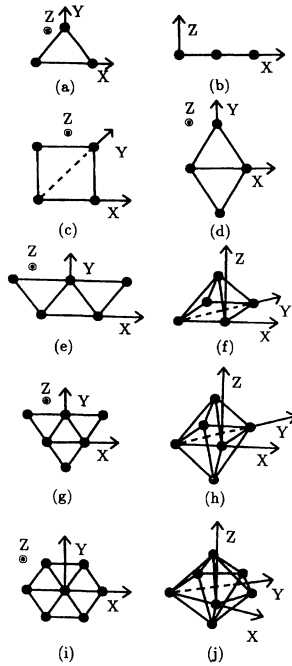


FIG. 3. Illustration of the cluster structures and the directions of the magnetization,  $x$ ,  $y$ , and  $z$ , considered in Table I.

phenomena in finite systems has been thus provided. While further extensions of this work are certainly worthwhile, the predictions of the present approach should always preserve their relevance due to the fundamental character of the unrestricted Hartree-Fock approximation and as a reference for future studies.

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TABLE I. Size and structural dependence of the magnetic anisotropy energy (MAE) of  $\text{Fe}_N$  clusters. The off-plane MAE  $E_x - E_z$  and the in-plane MAE  $E_x - E_y$  (results in brackets) are given in meV for different values of the interatomic bond length  $d$  ( $d_B$  is the bulk nearest-neighbor distance). The cluster structures and the directions of the magnetization  $x$ ,  $y$ , and  $z$  are illustrated in Fig. 3.

$N$ (struct.)	$d/d_B = 1.05$	$d/d_B = 1.00$	$d/d_B = 0.90$	
3	(a)	5.13 (1.43)	5.30 (1.01)	-0.11 (-0.10)
	(b)	2.01	1.69	1.25
4	(c)	5.02 (-0.48)	5.21 (-0.59)	-1.03 (-0.11)
	(d)	0.30 (-0.12)	0.27 (-0.12)	0.33 (0.31)
5	(e)	0.29 (-1.01)	0.28 (-0.82)	-0.10 (-0.75)
	(f)	1.09 (-0.01)	0.88 (-0.03)	-0.07 (0.04)
6	(g)	-1.25 (-0.76)	-1.12 (-0.62)	0.33 (0.29)
	(h)	4.66 (0.04)	4.82 (-0.02)	-0.07 (-0.23)
7	(i)	1.78 (0.40)	1.91 (0.09)	2.22 (0.30)
	(j)	4.32 (-0.03)	4.52 (-0.02)	-0.39 (0.00)

steps of this collaboration to be performed. This work has been financed in part by CONACyT (Mexico). G. M. P. also acknowledges the support provided by a fellowship of the J. S. Guggenheim Memorial Foundation.

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- [11] Let us recall that in the presence of SO interactions,  $S_z$  is no longer a good quantum number. Nevertheless, the mixing between different  $S_z$  is weak, except very close to changes in the spin polarization, where states of different  $S_z$  are quasidegenerate.
- [12] It is also worth mentioning that in a mean-field calculation at  $T = 0$  the discrete spin flips occur generally at slightly different values of  $d/d_B$  for different orientations of the magnetization  $\langle \vec{S} \rangle$ . In fact, close to a spin flip there are large peaks in the DOS of both spins located near  $\epsilon_F$ , which indicates that states of different spin are quasidegenerate [9]. Therefore, the SO corrections to the energy levels, though small, may modify the degeneracy of energy levels and their occupation at  $T = 0$  for different directions of the magnetization. This effect is detectable in a precise calculation like ours. However, we have omitted these points in Fig. 1, which would require a tedious analysis of the existence and stability of multiple solutions to the self-consistent equations. In addition, finite temperature effects would tend to smooth these transitions.