Co Dimers on Hexagonal Carbon Rings Proposed as Subnanometer Magnetic Storage Bits

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It is demonstrated by means of density functional and *ab initio* quantum chemical calculations, that transition-metal–carbon systems have the potential to enhance the presently available area density of magnetic recording by 3 orders of magnitude. As a model system, Co_2 benzene with a diameter of 0.5 nm is investigated. It shows a magnetic anisotropy of the order of 0.1 eV per molecule, large enough to store permanently 1 bit of information at temperatures considerably larger than 4 K. A similar performance can be expected, if cobalt dimers are deposited on graphene or on graphite.

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Long-term magnetic data storage requires that spontaneous magnetization reversals should occur significantly less often than once in ten years. This implies that the total magnetic anisotropy energy (MAE) of each magnetic particle should exceed $40kT$ [1], where k is the Boltzmann constant and T is the temperature. Among the elemental ferromagnets (Fe, Co, Ni, and Gd), cobalt metal shows the highest MAE, about 0.06 meV per atom. Thus, Co is the main ingredient of magnetic data storage materials at present. At room temperature, data loss due to fluctuations is avoided, if a Co grain contains not less than $40k \times 300\ \mathrm{K}/0.06\ \mathrm{meV} \approx 15\,000$ atoms. In fact, the grain diameter of contemporary $\mathrm{Co(Cr, Pt, SiO_2)}$ recording media is close to 8 nm, each grain containing about 50 000 atoms and each bit being composed of some dozen grains [2]. The grain size could be considerably reduced by using FePt or CoPt with MAE of almost 1 meV per atom in their structurally ordered $L1_0$ bulk phase. It is, however, hard to achieve the required ordered structure in nanoparticles [3].

Obviously, a further reduction of the bit size is limited by the value of MAE per atom. Recent efforts to enhance this value were focused on single atoms or small clusters on the surface of heavy metals [4]. This approach combines two ideas [5]: First, the magnitude of MAE is related to the size of the orbital moments. The latter are quenched for highly coordinated atoms but can be large if the coordination is low [6]. Second, the magnitude of MAE is related to the strength of spin-orbit coupling which grows with atomic number. Considerable progress was achieved in this way by deposition of single Co atoms on a Pt surface, yielding a record MAE of 9 meV per Co atom [7]. Unfortunately, clusters of several Co atoms on Pt show a much smaller MAE per atom, roughly inversely proportional to the number of atoms [7].

Free transition-metal clusters with 3…7 atoms were predicted to show large values of MAE in a pioneering tight-binding model calculation [8]. More recently, the magnetic properties of transition-metal dimers came into the focus of interest [9–12]. Isolated magnetic dimers are the smallest chemical objects that possess a magnetic anisotropy as their energy depends on the relative orientation between dimer axis and magnetic moment. Huge MAE values of up to 100 meV per atom were predicted by density functional (DFT) calculations for the cobalt dimer [9,10,12], confirming earlier model calculations [13].

Transition-metal dimers can routinely be produced [14]. It is impossible, however, to access the huge MAE of dimers unless they are bound to some medium. Chemical bonding, on the other hand, frequently spoils magnetism. A hitherto unanswered question is, can one find a substrate that does not deteriorate the dimer MAE. In the following, we will demonstrate by DFT and by *ab initio* quantum chemical calculations that carbon is a suitable host for subnanometer magnetic storage bits consisting of transition-metal dimers with exceptional magnetic anisotropy in the order of 0.1 eV.

An all-electron full-potential local-orbital scheme, FPLO-8.00-31 [15,16], was employed for the DFT calculations. The valence basis set comprised $3d$ transition metal ($3s$, $3p$, $3d$, $4s$, $4p$, $4d$, $5s$), $4d$ transition metal ($4s$, $4p$, $4d$, $5s$, $5p$, $5d$, $6s$), carbon ($1s$, $2s$, $2p$, $3s$, $3p$, $3d$), and hydrogen ($1s$, $2s$, $2p$) states. The presented data were obtained using the generalized gradient approximation (GGA) with a parameterized exchange-correlation functional according to Ref. [17]. A temperature broadening parameter of 100 K for the level occupation was used in the cluster mode and a mesh of $30 \times 30 \times 1$ **k**-points in the full Brillouin zone in the periodic mode (supercells with 26 Å height). Geometry optimization was carried out with a scalar-relativistic scheme. The MAE was obtained by means of self-consistent full-relativistic calculations. Resulting GGA data were regarded as a lower estimate for the expected MAE value. To get an upper estimate, an orbital polarization correction (OPC) [18,19] in the version proposed in Ref. [18] was applied to the cobalt $3d$ orbitals.

Co dimers have singly occupied twofold degenerate $3d$-δ orbitals which are responsible for the large dimer MAE [9,10]. This degeneracy is not lifted in a hexagonal environment. Thus, we have chosen to investigate the interaction between Co_2 and benzene (Bz, C_6H_6). The interaction of transition metals with Bz suitably models their adsorption onto graphite [20].

$Co_2C_6H_6$ has an even number of electrons and hence a spin magnetic moment of an even number of Bohr magnetons. To find out the lowest-energy geometry and spin magnetic state, five possible high-symmetry structures (Fig. 1) were optimized for each of the possible values of total spin moment, $\mu_s = 0, 2, 4,$ and $6\mu_B$. Different initial spin arrangements (ferro- and ferrimagnetic) were considered. The point group symmetry (C_{6v}, C_{2v}, or C_∞) as well as the geometry of the Bz were fixed in most calculations, since adsorption of transition metals on Bz has almost no influence on the C-C and C-H bond lengths [21]. This constraint was released when the influence of Jahn-Teller distortions was checked.

We find a binding energy of 1.39 eV for the Co_2 dimer to the Bz and a perpendicular orientation of the dimer axis to the Bz plane in the ground-state structure. We are not aware of previous investigations for this structure of $Co_2C_6H_6$. Perpendicular arrangement on Bz was evidenced before by spectroscopy on $Pd_2C_6H_6$ and $Pt_2C_6H_6$ [22]. Also, gold dimers were predicted to prefer a perpendicular orientation on graphene [23].

DFT calculations usually yield binding energies somewhat larger than related experimental values. Thus, to confirm the qualitative validity of the energies, structure sequence, and spin states of Fig. 1, we performed *ab initio* quantum chemical calculations. Binding energies were obtained from second order Møller-Plesset (MP2) perturbation theory as implemented in Gaussian03 [24]. The Co atoms were described by a scalar-relativistic effective core potential (ECP) replacing 10 core electrons (MDF10) [25], with the corresponding $(8s7p6d1f)/[6s5p3d]$ GTO basis set. For Bz the standard Dunning correlation-consistent double-zeta basis set (cc-pVDZ) [26] was used. All MP2 energies were evaluated from single point calculations using the DFT-derived geometries, except for the Co dimer. For the latter, the MP2 interatomic distance turned out slightly shorter (0.1909 nm) than the DFT result (0.1997 nm). Nonetheless, the binding energy of the Co dimer to Bz was found to be yet higher (2.67 eV) than in the DFT calculation. The perpendicular orientation of the dimer axis to the Bz plane was found to yield the lowest energy. The other configurations are separated from this structure by 1.40 eV, 2.11 eV, and 2.28 eV, respectively, in the sequence depicted in Fig. 1. The same ground-state spin magnetic moments as in the DFT calculations were found with the exception of the uppermost configuration, where a total moment of $2\mu_B$ was obtained by MP2 compared to $4\mu_B$ obtained by DFT. Thus, the quantum chemical calculations confirm the main DFT result, that bonding of a Co dimer with a single molecule of Bz results in the structure depicted at the bottom of Fig. 1 with a total spin magnetic moment of $4\mu_B$.

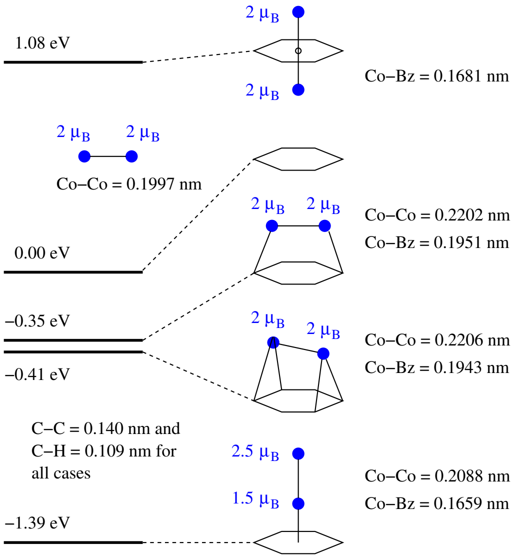

FIG. 1 (color online). DFT energies, interatomic distances, and ground-state spin magnetic moments of different Co_2-benzene configurations. The energies refer to the energy sum of free Co_2 and free Bz. Hexagons and blue bullets indicate Bz and Co, respectively. "Co-Bz" denotes the distance between the Bz plane and the nearest Co atom.

A compilation of related single-electron level schemes is given in Fig. 2. The rightmost panel shows the textbook electronic structure of Bz, while the leftmost panel refers to the free Co_2, as recently discussed in Refs. [9,10]. The two inner panels show our new results for the ground-state structure of Co_2Bz and for CoBz, included for comparison. The most important feature of the Co_2 level scheme is a twofold degenerate singly occupied $3d$-δ_u^* state. It is split by spin-orbit interaction (not shown), if the magnetic moment is oriented along the dimer axis but stays degenerate if the moment is perpendicular to the axis [9,10]. The related energy difference, the MAE, was predicted to be 28 to 50 meV per molecule [9,10,12]. This value should be considered as a lower estimate (L) to the expected MAE since it was evaluated without allowing for the so-called orbital polarization corrections. Rather an upper estimate (U), 188 meV per molecule [12], is obtained by including OPC.

Surprisingly, it turns out that bonding of Co_2 on Bz does not lead to any deterioration of its magnetic properties, but rather improves them: The spin moment stays $4\mu_B$, as in the free dimer. Noteworthy, any other spin state, including an antiferromagnetic solution with about $2\mu_B$ on each Co atom, has a much higher energy, at least 800 meV above the ground state. As a consequence, the $3d$-δ_u^* level is still singly occupied, Fig. 2. It is now further separated from the other levels than in the free dimer. Thus, while the lower estimate to MAE is hardly changed (51 meV per molecule), the upper one (330 meV per molecule) is even higher than in the free dimer. This huge MAE is accompanied by a large ground-state orbital moment, about $2\mu_B$

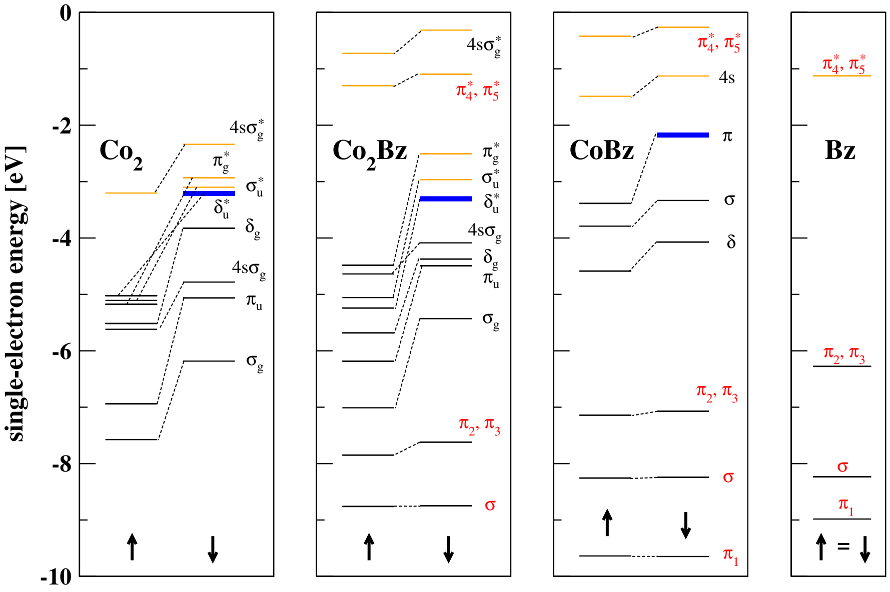

FIG. 2 (color online). Scalar-relativistic DFT single-electron levels of Co_2 (left panel), Co_2Bz (ground-state structure, second panel), CoBz (third panel), and Bz (right panel, $Bz = C_6H_6$). All energies refer to a common vacuum level. Black lines denote occupied states, orange lines denote empty states, and thick blue lines indicate singly occupied twofold degenerate states. With the exception of Bz, the levels are spin-split ($\mu_s = 4$, 4, and $1\mu_B$ for Co_2, Co_2Bz, and CoBz, respectively). Majority states are indicated by up arrows, minority states by down arrows. Co-like states are labeled in black and Bz-like states are labeled in red.

per molecule. The latter is largely suppressed if the total magnetic moment is directed parallel to the Bz plane. For this orientation, the $3d$-δ_u^* level is split by about 1 meV due to a tiny Jahn-Teller distortion of the Bz. The related reduction of MAE (less than 1 meV) is neglected in the presented results.

The CoBz molecule was earlier investigated both experimentally [27], by quantum chemical calculations [28], and by spin-polarized GGA [29], but its orbital magnetic behavior deserves further studies. Figure 2 shows the CoBz level scheme for its lowest spin state in the C_{6v} geometry with the Co atom 0.1501 nm above the center of the Bz ring. Here a $3d$-π doublet is singly occupied. Spin-orbit splitting of $3d$-π levels is smaller than that of $3d$-δ levels. Hence, we find somewhat smaller MAE values of 20 (L) and 90 (U) meV per Co atom. These numbers are comparable with the recently predicted MAE of 7.5 meV per tantalum atom (L) for TaBz [30].

Technological application of Co dimers might proceed via deposition of Co_2 on purified graphite. With this end in view, we have evaluated the properties of regular 3×3 arrangements of Co and of Co_2 on graphene as a model for the graphite (0001) surface. The results resemble those described for Bz: (i) the perpendicular orientation of Co_2 above the center of a carbon hexagon is preferred against any parallel orientation, including a position of the two Co atoms above two adjacent hexagons; (ii) single Co atoms prefer the hollow position as well; (iii) the binding energy is about 15% smaller than in the Bz case; (iv) both single Co atoms and Co dimers keep their essential electronic and magnetic features. Dissociation of the adsorbed Co dimer costs 2.79 eV if the Co atom escapes to the vacuum or 2.08 eV if it goes to a distant position on the graphene, respectively. These findings are consistent with recent pseudopotential results [31] where MAE was not considered and indicate stability of the Co dimers on graphene. Including spin-orbit coupling, we find that Co dimers on graphene show a magnetic anisotropy (L: 48, U: 320 meV per dimer) very similar to the Bz case, while the MAE of single Co atoms on graphene is somewhat reduced (L: 5, U: 40 meV per atom) in comparison to CoBz.

Figure 3 demonstrates the strong sensitivity of Co MAE to its environment and compares L and U to MAE with experimental data. While the U to MAE of Co_2 on C (0001), once confirmed by experiment, could guarantee 10-year stability of an information bit at the temperature of liquid nitrogen, even the lower estimate is a factor of 5 higher than the measured MAE of Co_2 on a Pt surface [7] and would provide the required stability at 12 K. A recent experiment demonstrated that single-molecule magnets can indeed be used for magnetic data storage: for Fe_4-organometallic complexes with an MAE of about

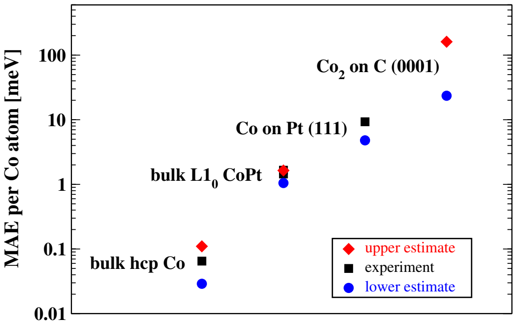

FIG. 3 (color online). Magnetic anisotropy energy of Co atoms in different chemical and structural environments. Black squares denote experimental data, blue circles and red diamonds denote lower and upper estimate theoretical data, as introduced in the text. Bulk hcp Co [34], bulk $L1_0$ CoPt [35], Co atoms on the Pt (111) surface (experiment [7] and theory [36]), and Co dimers on the graphite (0001) surface (our prediction) consecutively differ from each other by about 1 order of magnitude. There is no upper estimate available for Co on Pt (111), but a value of 74 meV has been found for Co on Ag (001) [37].

2 meV per molecule, an information decay time of about 200 s was measured at a very low temperature, 0.5 K [32].

Among all T_2-Bz molecules investigated in the present work (T = Fe, Co, Ni, Ru, Rh, Pd), Ru_2Bz is the only other interesting candidate for high MAE application. Ru_2 shows similarly good bonding behavior with Bz (energy and geometry) as the cobalt dimer and Ru_2Bz has an even higher L to MAE of 100 meV per molecule. However, the related magnetic ground state has a lower moment ($2\mu_B$) and lies only 250 meV below a state with zero moment. This situation is similar to a recently predicted effect termed "colossal magnetic anisotropy" in monatomic platinum nanowires [33] and deserves further investigation.

Summarizing, we predict that bonding of Co dimers on hexagonal carbon rings results in a perpendicular arrangement of the dimers with respect to the carbon plane and in a magnetic ground state. In this structure, a division of tasks takes place: while the Co atom closer to the carbon ring is responsible for the chemical bonding, the outer Co atom hosts the larger share of the magnetic moment. The huge magnetic anisotropy of the free dimer is preserved in this structure, since the degeneracy of the highest occupied $3d$-δ orbital is not lifted in a hexagonal symmetry. Thus, it should be possible to circumvent the hitherto favored use of heavy metal substrates to achieve large magnetic anisotropies. On the contrary, robust and easy-to-prepare carbon-based substrates are well suited for this task. Once confirmed, the present results may constitute an important step towards a molecular magnetic storage technology. Further necessary steps would include the fabrication of large regular arrays, the protection against oxidation without reducing the anisotropy, and the development of new read and write technologies.

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[1] S. H. Charap, P.-L. Lu, and Y. He, IEEE Trans. Magn. **33**, 978 (1997).

[2] T. Thomson, L. Abelman, and H. Groenland, *Magnetic Nanostructures in Modern Technology: Spintronics, Magnetic MEMS and Recording*, NATO Science for Peace and Security Series B-Physics and Biophysics (Springer, Heidelberg, 2008), chap. Magnetic data storage: Past present and future, p. 237.

[3] M. E. Gruner, G. Rollmann, P. Entel, and M. Farle, Phys. Rev. Lett. **100**, 087203 (2008).

[4] B. Lazarovits, L. Szunyogh, and P. Weinberger, Phys. Rev. B **65**, 104441 (2002).

[5] P. Bruno, Phys. Rev. B **39**, 865 (1989).

[6] R. A. Guirado-López, J. Dorantes-Dávila, and G. M. Pastor, Phys. Rev. Lett. **90**, 226402 (2003).

[7] P. Gambardella *et al.*, Science **300**, 1130 (2003).

[8] G. M. Pastor, J. Dorantes-Dávila, S. Pick, and H. Dreyssé, Phys. Rev. Lett. **75**, 326 (1995).

[9] T. O. Strandberg, C. M. Canali, and A. H. MacDonald, Nature Mater. **6**, 648 (2007).

[10] T. O. Strandberg, C. M. Canali, and A. H. MacDonald, Phys. Rev. B **77**, 174416 (2008).

[11] L. Fernández-Seivane and J. Ferrer, Phys. Rev. Lett. **99**, 183401 (2007).

[12] D. Fritsch, K. Koepernik, M. Richter, and H. Eschrig, J. Comput. Chem. **29**, 2210 (2008).

[13] J. Dorantes-Dávila and G. M. Pastor, Phys. Rev. Lett. **81**, 208 (1998).

[14] J. R. Lombardi and B. Davies, Chem. Rev. **102**, 2431 (2002).

[15] K. Koepernik and H. Eschrig, Phys. Rev. B **59**, 1743 (1999).

[16] http://www.fplo.de.

[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[18] O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 7311 (1990).

[19] H. Eschrig, M. Sargolzaei, K. Koepernik, and M. Richter, Europhys. Lett. **72**, 611 (2005).

[20] J. J. BelBruno, Surf. Sci. **577**, 167 (2005).

[21] R. Pandey, B. Rao, P. Jena, and M. Blanco, J. Am. Chem. Soc. **123**, 3799 (2001).

[22] G. Lüttgens, N. Pontius, C. Friedrich, R. Klingeler, P. S. Bechthold, M. Neeb, and W. Eberhardt, J. Chem. Phys. **114**, 8414 (2001).

[23] R. Varns and P. Strange, J. Phys. Condens. Matter **20**, 225005 (2008).

[24] M. J. Frisch *et al.*, Gaussian 03, Revision C.02 (Gaussian, Inc., Wallingford CT, 2004).

[25] M. Dolg, U. Wedig, H. Stoll, and H. Preuss, J. Chem. Phys. **86**, 866 (1987).

[26] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

[27] T. Kurikawa, H. Takeda, M. Hirano, K. Judai, T. Arita, S. Nagao, A. Nakajima, and K. Kaya, Organometallics **18**, 1430 (1999).

[28] C. W. Bauschlicher, Jr., H. Partridge, and S. R. Langhoff, J. Phys. Chem. **96**, 3273 (1992).

[29] R. Pandey, B. Rao, P. Jena, and J. M. Newsam, Chem. Phys. Lett. **321**, 142 (2000).

[30] Y. Mokrousov, N. Atodiresei, G. Bihlmayer, S. Heinze, and S. Blügel, Nanotechnology **18**, 495402 (2007).

[31] H. Johll, H. C. Kang, and E. S. Tok, Phys. Rev. B **79**, 245416 (2009).

[32] M. Mannini *et al.*, Nature Mater. **8**, 194 (2009).

[33] A. Smogunov, A. Dal Corso, A. Delin, R. Weht, and E. Tosatti, Nature Nanotech. **3**, 22 (2008).

[34] J. Trygg, B. Johansson, O. Eriksson, and J. M. Wills, Phys. Rev. Lett. **75**, 2871 (1995).

[35] P. Ravindran, A. Kjekshus, H. Fjellvåag, P. James, L. Nordström, B. Johansson, and O. Eriksson, Phys. Rev. B **63**, 144409 (2001).

[36] A. Mosca Conte, S. Fabris, and S. Baroni, Phys. Rev. B **78**, 014416 (2008).

[37] B. Nonas, I. Cabria, R. Zeller, P. H. Dederichs, T. Huhne, and H. Ebert, Phys. Rev. Lett. **86**, 2146 (2001).