

From the bulk to monatomic wires: An *ab initio* study of magnetism in Co systems with various dimensionality

Matej Komelj,^{1,2} Claude Ederer,³ James W. Davenport,¹ and Manfred Fähnle^{3,*}

¹Brookhaven National Laboratory, Center for Data Intensive Computing, Upton, New York 11973

²Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

³Max-Planck Institut für Metallforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

(Received 22 July 2002; published 30 October 2002)

A systematic *ab initio* study within the framework of the local-spin-density approximation including spin-orbit coupling and an orbital-polarization term is performed for the spin and orbital moments and for the x-ray magnetic circular dichroism (XMCD) spectra in hcp Co, in a Pt supported and a free standing Co monolayer, and in a Pt supported and a free standing monatomic Co wire. When including the orbital-polarization term, the orbital moments increase drastically when going to lower dimensionality, and there is an increasing asymmetry between the L_2 and L_3 XMCD signals. It is shown that spin and orbital moments can be obtained with good accuracy from the XMCD spectra via the sum rules. The $\langle T_z \rangle$ term of the spin sum rule is surprisingly small for the wires, and the reason for this is discussed.

DOI: 10.1103/PhysRevB.66.140407

PACS number(s): 75.30.-m, 75.90.+w

The modern methods to prepare nanostructured systems made it possible to investigate the influence of dimensionality on the magnetic properties. A central question thereby is how the qualitative behavior will change when going from two-dimensional to one-dimensional systems because it has been predicted that there is no long-range magnetic order at finite temperature in infinitely extended one-dimensional systems with short-range magnetic interactions. In the past, several experimental investigations of monolayer nanostripes of Fe on vicinal surfaces of W (Refs. 1, 2) or Cu (Ref. 3) have been performed, with a stripe width down to 1–10 nm. Most recently, Gambardella *et al.*⁴ succeeded in preparing a high density of parallel atomic chains along steps by growing Co on a high-purity Pt(997) vicinal surface in a narrow temperature range. The magnetism of the Co wires was investigated⁵ by the x-ray magnetic circular dichroism (XMCD). Below a blocking temperature a long-range magnetic ordering owing to the presence of anisotropy barriers was found on the time scale of the experiment. In Ref. 5 a simple model of exchange-coupled superparamagnetic clusters was applied (for a criticism of this model, see Ref. 6) to obtain the anisotropy energy from the shape of the magnetization curve above the blocking temperature and it appeared to be much larger than the one for a Co monolayer on Pt which, in turn, is much larger than the one of hcp Co. Accordingly, a large orbital moment of $0.68\mu_B$ per Co atom was found, the highest value ever reported for a 3d itinerant electron system.

So far, magnetism in quasi-one-dimensional systems was studied mainly in the insulating material CsNiF_3 , where the magnetic Ni ions are arranged along linear chains that are well separated from each other so that the interchain interaction is only 10^{-3} or less of the intrachain interaction. Because of the one-dimensional character of this spin system and the easy-plane anisotropy, magnetic solitons play an important role in the dynamical and thermodynamical behavior which has been investigated by neutron-scattering experiments.⁷ The discovery of magnetism in one-dimensional metallic systems opens up the chance to extend

the research in many respects. First, by considering various vicinal surfaces the distance between the steps and hence the chains can be modified so that the transition from the well-isolated chains to interacting chains can be studied. Second, it is possible to grow, e.g., biatomic wires along the steps and to manipulate the wire length, and to study the respective influence on magnetic properties. Finally, we expect that the damping of magnetic excitations is larger for metals than for insulators and especially large for one-dimensional metals, possibly leading to peculiar properties of the nonlinear spin excitations.⁸

The already existing *ab initio* calculations for monatomic transition-metal wires considered magnetic moments,^{9–13} exchange couplings,¹³ and magnetic anisotropies.^{11,12,14} It turned out¹² that in these one-dimensional systems the orbital correlations were essential and that the magnetic anisotropy and hence also the orbital moments could not be calculated reliably by the local-spin-density approximation (LSDA) in combination with spin-orbit (SO) coupling. Instead, a term correcting explicitly for the orbital correlations has to be added. It is one of the objectives of the present paper to work out the growing importance of the orbital correlations with decreasing dimensionality by calculating orbital (and spin) moments by the LSDA (Ref. 15) including SO coupling (in a self-consistent manner) without and with the orbital-polarization term¹⁶ which takes into account at least in part the orbital-correlation effects. The calculations are performed for Co atoms in hcp Co, in a Pt supported and in a free standing monolayer, and in a Pt supported and in a free standing monatomic wire. Another objective is to calculate the respective XMCD spectra and discuss the influence of dimensionality on the accuracy of the spin and orbital moments when these are obtained from the XMCD spectra via the sum rules.^{17,18} The applicability of these sum rules is always an important issue for the analysis of experimental XMCD spectra. It has been shown that it is critical for the surface of an Fe or Ni crystal¹⁹ or for the Pt atoms at the interface of a Co-Pt multilayer.²⁰ The question is whether it is even more critical for systems with further reduced dimensionality.

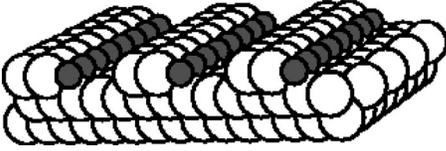


FIG. 1. The supercell used to model the monatomic Co wire on a vicinal Pt(997) surface.

To focus on the pure effect of the dimensionality we fix the nearest-neighbor distance of the atoms for all considered systems to the one of fcc Pt (2.77 Å). For the monolayers and wires we perform supercell calculations, i.e., large unit cells that model the structure are repeated periodically. In the case of the monolayer the supercell consists of two Pt and one Co {111} layers in the fcc stacking and a vacuum sheet corresponding to two empty layers. The vicinal Pt(997) surface with the Co wire at the steps is modeled by the supercell shown in Fig. 1 with two additional vacuum layers on the top. The supercell of the free standing wire is constructed by removing all Pt atoms from this supercell. Test calculations have shown that the results change only very slightly when going to larger supercells. For the monolayers and the wires we assume perpendicular magnetization, for hcp Co it is along the c axis.

We use the tight-binding linear-muffin-tin-orbital (LMTO) method in the atomic sphere approximation²¹ in which we have implemented the SO coupling and the tools for calculating the XMCD spectra, and the WIEN97 code²² which adopts the full-potential linearized-augmented-plane-wave (FLAPW) method²³ in which the SO coupling and the tools for the calculation of the magneto-optical effects and XMCD spectra^{24,25} and the orbital-polarization term²⁶ have been implemented. The magnetic orbital moments $m_l = -\mu_B \langle l_z \rangle$ and spin moments $m_s = -\mu_B \langle \sigma_z \rangle$ are calculated directly from the wave functions as well as via the sum rules^{17,18} from the absorption coefficients $\mu^+(\epsilon)$, $\mu^-(\epsilon)$, and $\mu^0(\epsilon)$ for light with right-circular, left-circular, and z -axis polarization at the L_2 and L_3 edges according to

$$\langle l_z \rangle = \frac{2I_m N_h}{I_t}, \quad (1)$$

TABLE I. The spin and orbital moments (in Bohr magnetons) as calculated from the LSDA without the orbital-polarization term (upper part) and with the orbital-polarization term (lower part). For the meaning of the various quantities, see text. The upper part gives also the $\langle T_z \rangle$ term appearing in the spin sum rule.

	hcp		Monolayer on Pt		Free monolayer		Wire on Pt		Free wire	
	LMTO	FLAPW	LMTO	FLAPW	LMTO	FLAPW	LMTO	FLAPW	LMTO	FLAPW
$\langle \sigma_z \rangle$ direct	1.83	1.83	2.03	2.00	2.02	2.12	2.21	2.06	2.22	2.16
$\langle \sigma_z \rangle$ d only	1.92	1.87	2.05	2.02	2.03	2.12	2.17	2.02	2.14	2.11
$\langle \sigma_z \rangle$ from Eq. (2)	1.79	1.88	1.96	2.12	2.03	2.18	2.09	2.13	2.14	2.36
$\langle \sigma_z \rangle$ from Eq. (2), $\langle T_z \rangle = 0$	1.80	1.86	1.50	1.77	1.58	1.62	1.76	1.94	2.28	2.26
$\langle T_z \rangle$	0.001	-0.003	-0.066	-0.050	-0.064	-0.079	-0.048	-0.027	0.021	-0.014
$\langle l_z \rangle$ direct	0.15	0.15	0.13	0.13	0.18	0.19	0.14	0.14	0.71	0.40
$\langle l_z \rangle$ from Eq. (1)	0.15	0.18	0.12	0.15	0.17	0.19	0.14	0.16	0.70	0.59
$\langle l_z \rangle$ direct		0.40		0.43		0.86		0.92		2.31
$\langle l_z \rangle$ from Eq. (1)		0.41		0.42		0.86		0.92		2.17

$$\langle \sigma_z \rangle = \frac{3I_s N_h}{I_t} - 7 \langle T_z \rangle, \quad (2)$$

$$I_m = \int_{E_F}^{E_c} [(\mu_c)_{L_3} + (\mu_c)_{L_2}] d\epsilon, \quad (3)$$

$$I_s = \int_{E_F}^{E_c} [(\mu_c)_{L_3} - 2(\mu_c)_{L_2}] d\epsilon, \quad (4)$$

$$I_t = \int_{E_F}^{E_c} [(\mu_t)_{L_3} + (\mu_t)_{L_2}] d\epsilon, \quad (5)$$

with the XMCD signal $\mu_c = \mu^+ - \mu^-$ and with $\mu_t = \mu^+ + \mu^- + \mu^0$. Here N_h is the number of d holes and $\langle T_z \rangle$ is the expectation value of the magnetic dipolar operator

$$\hat{T}_z = \frac{1}{2} [\boldsymbol{\sigma} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \boldsymbol{\sigma})]_z, \quad (6)$$

where $\boldsymbol{\sigma}$ denotes the vector of the Pauli matrices. The quantities E_F and E_c denote the Fermi energy and a cutoff energy. For details of such type of calculations see Ref. 20. The $\langle T_z \rangle$ term is negligible for cubic surroundings but it is expected to become more and more important when reducing the dimensionality of the system. Since it is very difficult to measure $\langle T_z \rangle$, this term is often neglected in the spin sum rule when analyzing the experimental data. One of the objectives of this paper is to assess this critically.

The results of the LSDA calculations with SO coupling are given in the upper part of Table I. It should be noted again that thereby we use the same nearest-neighbor distance between the atoms, i.e., the one of fcc Pt, for all structures. As explained in Ref. 20, the spin and orbital moments derived experimentally via the sum rules correspond essentially to the respective part of the valence wave functions with 3d angular momentum, if the “background” due to all additional contributions to the experimental absorption spectra is subtracted appropriately. We therefore compare in Table I the moments as calculated directly from the 3d spin and orbital densities with those obtained from the sum rules when taking into account for the absorption spectra and for the $\langle T_z \rangle$ term also only that part of the valence wave functions which has

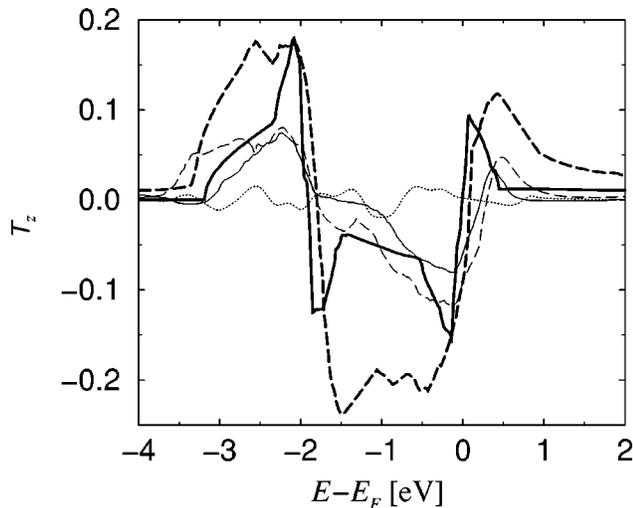


FIG. 2. The energy distribution of $\langle T_z \rangle$ for hcp Co (thin dotted line), a Co monolayer on Pt (thin dashed line), a free standing Co layer (thick dashed line), a monatomic Co wire on Pt (thin solid line), and a free standing monatomic Co wire (thick solid line).

3d character. For comparison, we give also the values of directly calculated moments including all angular momentum contributions.

For all the structures there is only a slight difference between the directly calculated moments with only d contributions and with all contributions. The spin moments increase only moderately with decreasing dimensionality. For the wire on Pt our directly calculated FLAPW spin value of $2.06\mu_B$ agrees well with the one of Ref. 10. There is also a satisfactory agreement between the directly calculated spin moments and those obtained from the spin sum rule when including the $\langle T_z \rangle$ term. The $\langle T_z \rangle$ contribution is negligible for hcp Co. In contrast, for the free and the Pt supported monolayers, the values of $\langle \sigma_z \rangle$ obtained from the sum rule when neglecting $\langle T_z \rangle$ are between 20% and 30% smaller than the directly calculated values. Astonishingly enough, when going to even stronger reduced dimensionality, i.e., for the Pt supported wire and even more for the free wire, the $\langle T_z \rangle$ term again appears to be of minor importance. To figure out the reason for this startling result, Fig. 2 shows the energy distribution¹⁹ for $\langle T_z \rangle$ for all the structures, i.e., the integral over the energy resolved contribution to $\langle T_z \rangle$ up to an energy E [for the integrals up to the Fermi level, $E = E_F$, $\langle T_z \rangle$ equals the quantity in Eq. (2)]. It becomes obvious that for the free standing monolayer and for the free standing wire, $\langle T_z \rangle$ depends drastically on E resulting in sharp structures in the energy distribution due to the two- or one-dimensional character of the systems. Going to the Pt supported monolayer and wire, the energy dependence of $\langle T_z \rangle$ is less pronounced and the sharp structures are smeared out, indicating that these systems are not really two- or one dimensional due to the presence of the substrate. However, $\langle T_z \rangle$ obtained from the integral up to E_F is very small for the free standing Co wire but larger for the other systems (except for hcp Co). This clearly demonstrates that the expected rule of thumb—a larger $\langle T_z \rangle$ for the smaller dimensionality—does not necessarily hold. We have performed the same calculation for a

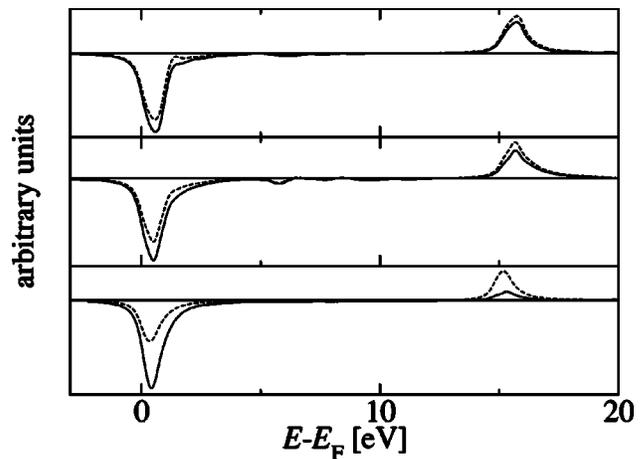


FIG. 3. The calculated XMCD spectra for hcp Co (upper part), Co monolayer on Pt (middle part), and Pt supported Co wire (lower part). The dashed (solid) lines show the result from the LSDA without (with) the orbital-polarization term.

free standing Ni wire. The energy distribution of $\langle T_z \rangle$ is very similar but the Fermi level is shifted and $\langle T_z \rangle$ is consequently much larger than for the Co wire. This again demonstrates that the symmetry arguments alone are not able to estimate the size of $\langle T_z \rangle$.

The orbital moments obtained by the LSDA calculation with SO coupling are very similar (about $0.15\mu_B$) for hcp Co and for the Pt supported Co monolayer and wire, while the values are slightly larger (about $0.18\mu_B$) for the free monolayer and considerably larger for the free wire. Thereby, there is a good agreement between the directly calculated orbital moments and those obtained from the calculated spectra via the sum rules. The rather small values for the Pt supported monolayer ($0.13\mu_B$) and the Pt supported wire ($0.14\mu_B$) are in conflict with the large corresponding experimental values⁵ ($0.31\mu_B$ and $0.68\mu_B$). As discussed in Ref. 12, the reason is presumably that LSDA + SO coupling does not appropriately account for orbital correlations. We therefore have redone all the calculations by including, in addition, the orbital-polarization term.¹⁶ Table I, lower part, gives the so obtained results for the orbital moments (the spin moments are nearly unaffected by this additional term). It should be noted that the calculations for hcp Co have been performed for the nearest-neighbor distance of fcc Pt, which explains the large moment of $0.4\mu_B$. For the Co monolayer on Pt (Co wire on Pt) our value $0.43\mu_B$ ($0.92\mu_B$) is even larger than the experimental value⁵ $0.31\mu_B$ ($0.68\mu_B$) which may be, in part, due to the fact that our calculations did not take into account any structural relaxations at the surface. For the free standing wire, the orbital moment appears to be extraordinarily high ($2.3\mu_B$). According to Ref. 27 this high orbital moment is very likely explained in terms of the lack of crystal-field charges that break the rotational symmetry of the wires. Obviously the experimental trend—increase of the orbital moment with decreasing dimensionality—is well reproduced when taking into account the orbital-polarization term. The increasing orbital moments result in an increasing asymmetry between the calculated L_2 and L_3 XMCD spectra (Fig. 3),

in qualitative agreement with the respective experimental spectra (Fig. 2 of Ref. 5).

Both, for the LSDA calculations with and without the orbital-polarization term, the directly calculated orbital moments agree very well with those obtained from the sum rule. Therefore, for Co in structures of various dimensionality the spin and orbital moments probably may be obtained with high accuracy from the sum rules (if including the $\langle T_z \rangle$ term in the spin sum rule).

In conclusion, we have shown that the orbital correlations have to be taken into account explicitly in order to reproduce the experimentally observed trend to higher orbital moments and larger asymmetries between the L_3 and L_2 XMCD spec-

tra in Co systems with reduced dimensionality, and we are about to do this also for a systematic study of the magnetic anisotropy. In addition, we calculate *ab initio* the further parameters appearing in a model Hamiltonian for the monatomic wires, i.e., exchange interactions from the adiabatic spin-wave spectra,²⁸ and the Gilbert damping factor.²⁹ The final objective is to provide a comprehensive description of the thermodynamic properties (see Ref. 6) and of the damped nonlinear excitations (along the lines of Ref. 8) of monatomic magnetic linear chains.

The work at Brookhaven was supported by U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

-
- *Electronic address: faehn@physix.mpi-stuttgart.mpg.de. <http://physix.mpi-stuttgart.mpg.de/schuetz/elth/electronth.html>
- ¹H.J. Elmers, J. Hauschild, H. Höche, U. Gradmann, H. Bethge, D. Heuer, and U. Köhler, *Phys. Rev. Lett.* **73**, 898 (1994).
 - ²J. Hauschild, H.J. Elmers, and U. Gradmann, *Phys. Rev. B* **57**, R677 (1998).
 - ³J. Shen, R. Skomski, M. Klaua, H. Jenniches, S. Sundar Manoharan, and J. Kirschner, *Phys. Rev. B* **56**, 2340 (1997).
 - ⁴P. Gambardella, M. Blanc, L. Bürgi, K. Kuhnke, and K. Kern, *Surf. Sci.* **449**, 93 (2000).
 - ⁵P. Gambardella, A. Dallmeyer, K. Maiti, M.C. Malagoli, W. Eberhardt, K. Kern, and C. Carbone, *Nature (London)* **416**, 301 (2002).
 - ⁶In this model the size of the superparamagnetic “particles” is estimated from the time-dependent kink density of the one-dimensional nearest-neighbor-exchange model in the infinite anisotropy (i. e., Ising) limit. Then these particles are considered as decoupled from each other but exposed to an external magnetic field and an anisotropy field, and the thermodynamics is described by classical Boltzmann statistics. In reality, the exchange energy is certainly much larger than the anisotropy energy also for the monatomic wires, and therefore the wire sections cannot be considered as decoupled, see, e.g., J. Shen *et al.*, *Phys. Rev. B* **56**, 2340 (1997). Therefore, it would be highly desirable to have a more rigorous treatment by calculating the dynamical structure factor for a one-dimensional chain with finite magnetic anisotropy and external magnetic field.
 - ⁷H.-J. Mikeska and M. Steiner, *Adv. Phys.* **40**, 191 (1991).
 - ⁸J.A. Holyst, A. Sukiennicki, and J.J. Żebrowski, *Phys. Rev. B* **33**, 3492 (1986).
 - ⁹M. Weinert and A.J. Freeman, *J. Magn. Magn. Mater.* **38**, 23 (1983).
 - ¹⁰G. Bihlmayer, X. Nie, and S. Blügel (unpublished) referred to in Ref. 5.
 - ¹¹J. Dorantes-Dávila and G.M. Pastor, *Phys. Rev. Lett.* **81**, 208 (1998).
 - ¹²L. Zhou, D. Wang, and Y. Kawazoe, *Phys. Rev. B* **60**, 9545 (1999).
 - ¹³D. Spišák and J. Hafner, *Phys. Rev. B* **65**, 235405 (2002).
 - ¹⁴M. Eisenbach, B.L. Györfy, G.M. Stocks, and B. Újfalussy, *Phys. Rev. B* **65**, 144424 (2002).
 - ¹⁵J.P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
 - ¹⁶O. Eriksson, M.S.S. Brooks, and B. Johansson, *Phys. Rev. B* **41**, 7311 (1990).
 - ¹⁷B.T. Thole, P. Carra, F. Sette, and G. van der Laan, *Phys. Rev. Lett.* **68**, 1943 (1992).
 - ¹⁸P. Carra, B.T. Thole, M. Altarelli, and X. Wang, *Phys. Rev. Lett.* **70**, 694 (1993).
 - ¹⁹R. Wu, D. Wang, and A.J. Freeman, *J. Appl. Phys.* **75**, 5802 (1994).
 - ²⁰C. Ederer, M. Komelj, M. Fähnle, and G. Schütz, *Phys. Rev. B* **66**, 094413 (2002).
 - ²¹O.K. Andersen and O. Jepsen, *Phys. Rev. Lett.* **53**, 2571 (1984).
 - ²²P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, *Comput. Phys. Commun.* **59**, 399 (1990).
 - ²³E. Wimmer, H. Krakauer, M. Weinert, and A.J. Freeman, *Phys. Rev. B* **24**, 864 (1981).
 - ²⁴J. Kuneš, P.M. Oppeneer, H.-C. Mertins, F. Schäfers, A. Gaupp, W. Gudat, and P. Novák, *Phys. Rev. B* **64**, 174417 (2001).
 - ²⁵J. Kuneš, P. Novák, M. Diviš, and P.M. Oppeneer, *Phys. Rev. B* **63**, 205111 (2001).
 - ²⁶C.O. Rodriguez, M.V. Ganduglia-Pirovano, E.L. Peltzer y Blancá, M. Petersen, and P. Novák, *Phys. Rev. B* **63**, 184413 (2001).
 - ²⁷R. Skomski and J. M. D. Coey, *Permanent Magnetism* (Institute of Physics, Bristol, 1999).
 - ²⁸O. Grotheer, C. Ederer, and M. Fähnle, *Phys. Rev. B* **63**, 100401 (2001).
 - ²⁹T.L. Gilbert, *Phys. Rev.* **100**, 1243 (1955).