Comment on ''Ultrathin Mn films on Cu(111) substrates: Frustrated antiferromagnetic order''

Ph. Kurz, G. Bihlmayer, and S. Blügel*
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

K. Hirai
Department of Physics, Nara Medical University, Kashihara, Nara 634-8521, Japan

T. Asada
Faculty of Engineering, Shizuoka University, Hamamatsu 432-8561, Japan
(Received 20 June 2000; published 6 February 2001)

We have studied collinear and noncollinear magnetic structures of a Mn monolayer on Cu(111) by use of the generalized gradient approximation to the density-functional theory using the full-potential linearized augmented plane-wave method. We found that the inclusion of the gradient correction did not significantly modify earlier results obtained in the local-density approximation. Irrespective of the choice of the exchange correlation functional, among the magnetic structures investigated, the minimal energy was found for a collinear row-wise antiferromagnetic structure. Our findings are at clear variance with a recent first-principles study [Phys. Rev. B **61**, 12 728 (2000)], which reported that Mn on Cu(111) exhibits a noncollinear ground state with magnetic moments forming $\pm 120°$ angles between nearest neighbors, claiming that this is due to the generalized gradient approximation essential in these systems. We discuss this point in detail. From our investigation of the zero-temperature phase diagram of the Heisenberg model going beyond nearest-neighbor interaction, we argue that it is not possible to determine the magnetic ground state from an investigation of a limited set of three different magnetic states, but a full investigation of spiral spin-density waves is required.

DOI: 10.1103/PhysRevB.63.096401 PACS number(s): 75.70.Rf, 75.70.Ak, 75.30.Fv, 71.15.Ap

In a recent paper, Spišák and Hafner (SH) (Ref. 1) investigated the magnetism of a Mn film of one monolayer (ML) thickness on Cu(111) performing *ab initio* calculations using the noncollinear spin-polarized real-space tight-binding linear muffin-tin orbital (RS-TB-LMTO) technique developed in their group. Exchange and correlation have been described by the local-spin-density functional of Ceperley and Alder[2] as parametrized by Perdew and Zunger,[3] adding generalized gradient corrections in the form proposed by Perdew and Wang.[4,5] Three different magnetic states had been considered. The two magnetic states with the lowest energy and thus most relevant in this context here, are (a) the row-wise antiferromagnetic (RW-AFM) state with two atoms per unit cell [cf. Fig. 1(a)] and (b) a two-dimensional noncollinear 120° structure with three atoms in a $(\sqrt{3}\times\sqrt{3})R30°$ surface unit cell of coplanar spins forming $\pm 120°$ angles between nearest neighbors [cf. Fig. 1(b)]. SH concluded that (i) the magnetic ground state of Mn/Cu(111) is the 120° state, and (ii) that the Mn/Cu(111) is a physical realization of the antiferromagnetic planar model[6,7] (AFP) on a triangular lattice. Both findings are clearly at variance with our first-principles results (hereafter cited as OUR) for an unsupported (freestanding) Mn(111) monolayer (UML) in the lattice constant of Cu as well as for a supported monolayer of Mn/Cu(111) published in Ref. 8. Our results had been obtained in the local-spin-density approximation (LSDA) of Moruzzi, Janak, and Williams.[9] SH stated in Ref. 1 that (iii) the discrepancy between OUR results and the results of SH ''… is clearly due to their neglect of gradient corrections …''. It is further stated that (iv) ''the use of the gradient corrections is essential …''. These statements as well as the conclusions (i) and (ii) are very surprising in the light of their investigation: (1) The 120° state is only 1.9 meV higher than the RW-AFM state, which is a very small quantity. (2) The sequence of the energies is not consistent with the densities of states (DOS) published by SH. (3) SH have not given evidence that the neglect of the generalized gradient approximation (GGA) changes the energy sequence of the magnetic states, in particular as little is known about the role of the GGA on antiferromagnets in low dimensions. (4) As we will show below, the calculation of only three magnetic states are by far not sufficient to conclude on the magnetic ground state of antiferromagnets on a triangular lattice.

In our previous work[8] we investigated collinear and noncollinear magnetic structures of Cr and Mn monolayers on a Cu(111) substrate. The calculations are carried out with the full-potential linearized augmented plane-wave (FLAPW) method in film geometry[10] as implemented in the program FLEUR. The method has been extended to treat noncollinear magnetism with magnetic moments M^α at atom sites α oriented along arbitrarily chosen directions $\{\hat{\mathbf{e}}_M^\alpha\}$. The potential, magnetic fields, and charge and magnetization densities are treated without any shape approximation and the magnetization density $\mathbf{m}(\mathbf{r})$ is a vector quantity which we treat similar to Nordström and Singh:[11] the full continuous vector magnetization density $\mathbf{m}(\mathbf{r})$ is used in the interstitial region between the atoms and in the vacuum region. Around each atom α a (muffin-tin) sphere is defined in which, in deviation to Nordström and Singh, the magnetization density has only one local magnetization axis,[12] $\mathbf{m}_\alpha(\mathbf{r})\approx m_\alpha(\mathbf{r})\hat{\mathbf{e}}_M^\alpha$. The integral of $m(\mathbf{r})$ over the sphere defines a local moment $M_\alpha = \langle m_\alpha \rangle$ as average magnetization along $\hat{\mathbf{e}}_M^\alpha$. In general (except for some high-symmetry magnetic states, e.g., the fer-

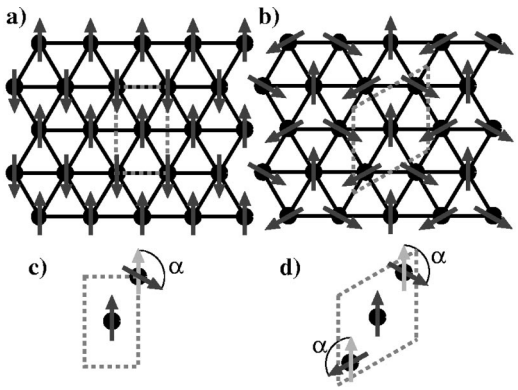

FIG. 1. (a) The RW-AFM structure. (b) The noncollinear 120° configuration. The ferromagnetic structure can be transformed by a continuous rotation into structure (a) as indicated in (c) and into structure (b) as indicated in (d).

romagnetic state), the magnetization directions $\hat{\mathbf{e}}_M^\alpha$ are not extrema to the total-energy functional $E[n(\mathbf{r}),\mathbf{m}(\mathbf{r})]$. To ensure that the local moments have no components $M_\perp^\alpha$ normal to the directions $\hat{\mathbf{e}}_M^\alpha$, $\hat{\mathbf{e}}_\perp^\alpha$, we work with the constrained density-functional theory[13] in which the total energy for a set of prescribed directions $E(\{\hat{\mathbf{e}}_M^\alpha\})$ is solved subject to the orientational constraint of the magnetic moments, that $\langle \mathbf{m}^\alpha \rangle \times \hat{\mathbf{e}}_M^\alpha$ is zero for all atoms,

$$E(\{\hat{\mathbf{e}}_M^\alpha\}) = \min\left\{ E[n(\mathbf{r}),\mathbf{m}(\mathbf{r})] + \sum_\alpha \mathbf{B}_\perp^\alpha \cdot \langle \mathbf{m}^\alpha \rangle \times \hat{\mathbf{e}}_M^\alpha \right\}. \tag{1}$$

The Lagrange multipliers $\mathbf{B}_\perp^\alpha$ are transverse constraining fields in the direction $\hat{\mathbf{e}}_\perp^\alpha$ that are obtained self-consistently. The effective B field, $\mathbf{B}_{eff}^\alpha(\mathbf{r})$, that enters the muffin-tin part of the Hamiltonian is an $\mathbf{r}$-dependent vector B field and is given by the B field due to the exchange and correlation, $B_{xc}(\mathbf{r})$, in the direction of $\hat{\mathbf{e}}_M^\alpha$ and the constraining field

$$\mathbf{B}_{eff}^\alpha(\mathbf{r}) = B_{xc}^\alpha(\mathbf{r})\,\hat{\mathbf{e}}_M^\alpha + B_\perp^\alpha \hat{\mathbf{e}}_\perp^\alpha = B_{eff}^\alpha(\mathbf{r})\,\hat{\mathbf{e}}_B^\alpha(\mathbf{r}). \tag{2}$$

More details on the implementation will be published in a forthcoming paper.[14] We think that this is currently one of the most accurate *ab initio* methods for the treatment of noncollinear magnetism of itinerant magnets in low dimensions. In particular, this approach allows the investigation of the functional behavior of $E(\{\hat{\mathbf{e}}_M^\alpha\})$ and thus a direct test of the underlying model Hamiltonians.

Constraining the magnetic moments along orientations described by an angle α in the two-atom (2AT) [see Fig. 1(c)] and three-atom (3AT) unit cell [see Fig. 1(d)], we calculated the total energies $E(\alpha)$. The angle α was varied in small steps, which generated a path of quasicontinuously varying orientations connecting high-symmetry magnetic states, i.e., the ferromagnetic (FM) with the RW-AFM [Fig. 1(a)] state, or connecting the FM state with the 120° state [Fig. 1(b)] and with a collinear (anti)ferrimagnetic state (FI) at $\alpha = 180°$ in the corresponding 2AT and 3AT unit cells. In the view of the rather large sets of spin configurations we have worked first with unsupported (free-standing) monolayers (UML) on the hexagonal lattice with the Cu lattice constant. Since the hybridization between a transition-metal overlayer and a noble-metal substrate is small, the UML represent an excellent model for monolayers on noble-metal substrates. The main conclusion of this investigation was that: (i) in contradiction to the AFP model, the 120° configuration on the triangular lattice is not the lowest energy configuration. Instead, among all magnetic states investigated, characterized by the angle α in the 2AT and 3AT unit cell, the lowest energy configuration of Mn(111) in the Cu lattice constant is the RW-AFM state and (ii) at present we cannot rule out whether a more complex configuration with a lower energy exists.

TABLE I. Energy differences relative to the RW-AFM state in meV/atom for the 120° and the FM state. Compared are the Mn monolayers as UML calculated the LSDA using the theoretical LSDA lattice constant of Cu (6.65 a.u.) and the ML on Cu(111) calculated in the LSDA and the GGA using the theoretical GGA lattice constant of Cu (6.82 a.u.).

	UML-LSDA	ML-LSDA	ML-GGA
120° − RW-AFM	68	77	89
FM−RW-AFM	358	261	296

The calculations of the UML's reported in OUR paper had been carried out for the theoretical L(S)DA lattice constant of Cu, $a_0 = 6.65$ a.u., and the geometry of the Cu(111) surface. The calculations were based on the local-spin-density approximation of von Barth and Hedin,[15] but with parameters as chosen by Moruzzi, Janak, and Williams.[9] The results are collected in Table I. We find that among all magnetic states in the 2AT and 3AT unit cells characterized by the angle α, the RW-AFM state is the lowest in energy. We find that the 120° state is 68 meV higher and the FM state is 358 meV higher in energy than the RW-AFM state. We carefully investigated the reliability of the total-energy differences with respect to the number of $\mathbf{k}_\parallel$-points used in the two-dimensional Brillouin zone (2DBZ). A $\mathbf{k}_\parallel$-point set that corresponds to 500 $\mathbf{k}_\parallel$-points in the full 2DBZ has been used for the unit cell containing two atoms, while the $\mathbf{k}_\parallel$-point set for the $(\sqrt{3}\times\sqrt{3})R30°$ unit cell corresponds to 361 $\mathbf{k}_\parallel$-points in the full 2DBZ. Both *k*-point sets correspond to about 1000 $\mathbf{k}_\parallel$-points in the 2DBZ of the $p(1\times1)$ unit cell. It has been checked very carefully that the total-energy differences calculated in the two different unit cells are comparable (in particular with respect to the $\mathbf{k}_\parallel$-point convergence), by comparing the energy difference between the nonmagnetic and ferromagnetic configurations in both unit cells.

SH claimed (iii) that the difference between the two results are due to the neglect of the generalized gradient approximation (GGA) in OUR calculations. Therefore, we have recalculated the FM, RW-AFM, and the 120° state applying the GGA of Perdew and Wang[16] (PW91). First, the theoretical Cu bulk lattice constant was determined to be 6.82 a.u., slightly larger than the experimental value of 6.81 a.u. Next, we determined the interlayer relaxation of a ferromagnetic Mn ML on Cu(111). The system was modeled by a

symmetric nine-layer film consisting of a seven-layer Cu(111) film and 1ML Mn on top of each Cu surface. We allowed all layers to relax and minimize the forces exerted on the atoms. We found that the Mn overlayer expands almost 5% outwards, and also the inner Cu interlayer distances are affected by this expansion. The result of this structural optimization has been used for all three magnetic structures investigated. Then, we recalculated the total energies and the magnetic moments for the three magnetic states for 1ML Mn/Cu(111). The system was modeled by an asymmetric five-layer film consisting of 4 layers of Cu and 1ML Mn on only one side of the Cu surface. The calculation has been carried out using a *k*-point set that corresponds to 1024 $\mathbf{k}_{\|}$ points in the full 2DBZ of a $p(1\times1)$ unit cell. We found that even with substrate, in the geometric structure optimized by force calculations within GGA, the LSDA finds that the RW-AFM is the lowest magnetic state among the three magnetic states, 77 meV lower in energy than the 120° state and 261 meV lower than the FM state. Then, we have repeated the calculation using the GGA. Although GGA changes the energy differences slightly between the various states, the results do not change qualitatively (see Table I). Concerning the merit of the GGA to the structure and magnetism of 3*d* transition metals, we would like to add the following comment on point (iv), that the GGA is essential in these investigations because the LSDA leads to the incorrect ground state of Mn: The GGA improves greatly the lattice constants and the magnetic energies of 3*d* transition metals,[17] but to gain this merit one has to calculate the exchange and correlation potential beyond the atomic sphere approximation (ASA), where the charge density is spherically averaged inside a sphere around an atom as it is typically done in the RS-TB-LMTO method. Compared to results calculated with a full-potential method, the ASA approximation overestimates, for example, the lattice parameters for Fe as discussed in Refs. 17–19 but underestimates the magnetic energies of Fe by 50 meV. On the other hand, Singh and Ashkenazi[20] found out that the GGA, although improving the bulk Cr lattice constant, yields far too large magnetic moments that might spoil the predictive power of GGA calculations on Cr and antiferromagnets in general. In our opinion it is not so evident that the GGA is so essential for the magnetism of antiferromagnets in low dimensions as long as the lattice constant is chosen properly, particularly if a method is used which relies on the ASA approximation.

At present we cannot resolve the difference between the two results. One possible source of error might be that the RW-AFM and the 120° state are calculated in two different unit cells, one containing 8 atoms and one 9 atoms per layer. How an absolute convergence of the total energy in different unit cells was achieved was not shown. However, SH presented the DOS for the three different spin configurations investigated. At the DOS of the 120° state we notice a very sharp peak right at the Fermi energy. Usually such a sharp peak at the Fermi energy makes the corresponding magnetic state rather unfavorable and is often the origin of an instability. On the other hand the DOS of the RW-AFM state exhibits a minimum at the Fermi energy, which is typically a sign of energetic stability. Why this elementary physical picture is not consistent with the total-energy results of SH should be a matter of further investigations.

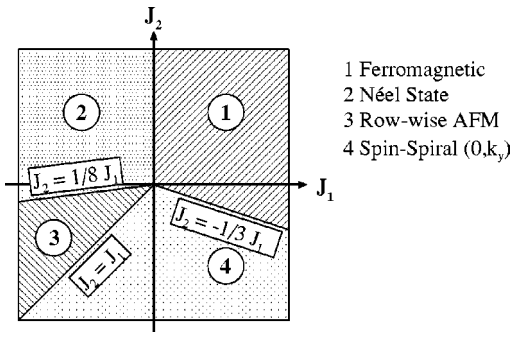

FIG. 2. Zero-temperature phase diagram in the (J_1, J_2) space indicating the regions of the four possible magnetic states.

At the end we would like to discuss the possible magnetic ground state of Mn/Cu(111). In order to gain insight into the nature of the problem discussing a model is a good starting point. One of the simplest spin models is the AFP (Ref. 6) model specified by the following Hamiltonian:

$$H=-J_1\sum_{\langle ij\rangle}\mathbf{S}_i\mathbf{S}_j, \tag{3}$$

where $J_1<0$ describes the antiferromagnetic exchange interaction between classical planar spin-vectors at site *i* and *j*, restricted to nearest-neighbor pairs $\langle ij\rangle$. On a triangular lattice the ground state is either the 120° or the FM state ($J_1>0$). Thus in the light of our results this model is insufficient. The fact that the RW-AFM state is lower in energy than the 120° state suggests that long-range interactions play an important role. This is reasonable since Mn is an itinerant magnet where electrons responsible for the magnetism hop across the lattice. In Fig. 2 we show a zero-temperature phase diagram calculated in the (J_1,J_2) space. An extension of the AFP model to the Heisenberg model with exchange interactions between spins at nearest and next-nearest (J_2) neighbors gives four possible magnetic ground states: FM, RW-AFM, 120°, and the spiral spin-density wave (SSDW). The magnetic ground state depends on the sign and magnitude of the different *J*'s. We obtain the 120° state under the condition that $J_1<0$ and $J_2>\frac{1}{8}J_1$, the RW-AFM state for $J_1<0$ and $\frac{1}{8}J_1>J_2>J_1$, and the SSDW state for $J_2<J_1$ and $J_2<-\frac{1}{3}J_1$. Since our calculations show that the exchange interactions beyond the nearest neighbors are important, any discussion on the magnetic ground state of a Mn monolayer on Cu(111) remains inconclusive prior to the investigation of the SSDW, which nobody has done so far for ultrathin films.

As a final point, we would like to mention what could be deduced from the calculated functional form of $E_{3AT}(\alpha)$. Within the AFP model, $E_{3AT}(\alpha)$ is given as $E_{3AT}(\alpha)=-2J_1(2\cos\alpha+\cos 2\alpha)$. This is not in agreement with the functional form of $E_{3AT}(\alpha)$ we found in Ref. 8 and cannot even be corrected including any long-range interaction of the Heisenberg model. Therefore, it is even not clear whether the Heisenberg model is appropriate to describe the magnetic ground state of Mn on Cu(111) and that the ground state is one of the four magnetic states discussed above.

In summary we found that for 1ML Mn/Cu(111) the RW-AFM state has the lowest energy among all magnetic states investigated so far, irrespective of the choice of the exchange correlation potential. We think that these results are very reliable as the method is optimally suited to deal with noncollinear magnetism of transition metals in low dimensions. In addition our results are consistent to the DOS presented by SH. We presented arguments that the present choice of investigated magnetic structures are insufficient to conclude that the RW-AFM is the magnetic ground state prior to the investigation of spin-spiral states along the high-symmetry lines of the 2DBZ. A thorough test of the accuracy of the RS-TB-LMTO method in comparison to a full-potential all-electron method is missing in the literature, but seems highly desirable. During the completion of the manuscript we noticed that Hobbs and Hafner,[21] now using a noncollinear projector augmented wave method within the GGA, found also that for Mn on Cu(111) the RW-AFM structure is more stable than the Néel state. Unfortunately, neither LDA nor SSDW-state calculations have been reported nor the differences between the two results have been explained or analyzed in detail.

This work was supported by the DFG under Grant No. BL444/1-1 and the TMR Networks Contract No. FMRX-CT98-0178.

*Electronic address: S.Bluegel@fz-juelich.de

[1] D. Spišák and J. Hafner, Phys. Rev. B **61**, 12 728 (2000).
[2] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[3] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[4] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[5] Unfortunately, Ref. 4 does not discuss the gradient corrections. Therefore, it is not known exactly which gradient correction has been chosen.
[6] D.H. Lee, J.D. Joannopoulos, J.W. Negele, and D.P. Landau, Phys. Rev. B **33**, 450 (1986).
[7] Please notice that the antiferromagnetic planar (AFP) model defined in Ref. 6 and used in SH (Ref. 1) are not the same. In Ref. 6 the AFP is restricted to the nearest-neighbor interaction and only two different periodic magnetic ground-state solutions exist, the ferromagnetic and the 120° state depending on the sign of the exchange interaction. In the AFP-SH model in Ref. 1 the restriction to the nearest-neighbor interaction is lifted and the interaction between pairs of spins at arbitrary atom sites are included. We think that this version of the AFP model is a more realistic description of the itinerant nature of a transition-metal monolayer, but in opposition to the statement made by SH the ground state of the AFP-SH is not necessarily the 120° state, but very complex spin states may arise.
[8] T. Asada, G. Bihlmayer, S. Handschuh, S. Heinze, Ph. Kurz, and S. Blügel, J. Phys.: Condens. Matter **11**, 9347 (1999).
[9] V.L. Moruzzi, J.F. Janak, and A.R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).
[10] E. Wimmer, H. Krakauer, M. Weinert, and A.J. Freeman, Phys. Rev. B **24**, 864 (1981); M. Weinert, E. Wimmer, and A.J. Freeman, *ibid.* **26**, 4571 (1982).
[11] L. Nordström and D.J. Singh, Phys. Rev. Lett. **76**, 4420 (1996).
[12] This is an excellent approximation for 3*d* transition metals.
[13] P.H. Dederichs, S. Blügel, R. Zeller, and H. Akai, Phys. Rev. Lett. **53**, 2512 (1984).
[14] Ph. Kurz, F. Förster, L. Nordström, G. Bihlmayer, and S. Blügel (unpublished).
[15] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[16] J.P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Academic Verlag, Berlin, 1991).
[17] M. Asato, A. Settels, T. Hoshino, T. Asada, S. Blügel, R. Zeller, and P.H. Dederichs, Phys. Rev. B **60**, 5202 (1999).
[18] D.J. Singh, W.E. Pickett, and H. Krakauer, Phys. Rev. B **43**, 11 628 (1991).
[19] K.B. Hathaway, H.J.F. Jansen, and A.J. Freeman, Phys. Rev. B **31**, 7603 (1985).
[20] D.J. Singh and J. Ashkenazi, Phys. Rev. B **46**, 11 570 (1992).
[21] D. Hobbs and J. Hafner, J. Phys.: Condens. Matter **12**, 7025 (2000).