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Ferromagnetism versus antiferromagnetism of the Cr(001) surface

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Three different spin arrangements for the (001) surface of Cr are discussed on the basis of self-consistent total-energy calculations: ferromagnetism, inside-the-surface $c(2\times2)$ antiferromagnetism, and "topological" antiferromagnetism between ferromagnetic terraces separated by single steps. The $c(2\times2)$ antiferromagnetic configuration is found to be energetically unfavorable. Instead, topological antiferromagnetism is compatible with both the absence of magnetization observed by spin-resolved photoemission and the existence of spin-split surface states detected by energy- and angular-resolved photoemission.

In recent years solid-state physics has witnessed an intense research on the magnetism of 3*d* transition-metal surfaces and thin films, which led to a considerable progress in our understanding of surface magnetic properties. Theoretical efforts focused upon the (100) surfaces of Fe, Ni, Cr, and V.[1] Using most sophisticated self-consistent total-energy calculations, the persistence of ferromagnetic order up to the very surface layer of ferromagnetic Fe and Ni has been established. Most intriguingly, a 20%–30% *enhancement* of the magnetic moments at the surface was found, which is now understood as an effect of the reduced coordination number causing band narrowing and reduced *s*-*d* hybridization.

The Cr(001) surface occupies a unique place. In contrast to Fe and Ni, bulk Cr has an antiferromagnetic (AF) ground state, which results from an incommensurable spin-density wave, with periodicity of about two lattice spacings,[2] pointing in a [001] direction. The moment per atom is $0.59\mu_B$. This AF picture leads roughly to alternating (001) planes with spins inside each plane pointing in the same direction—a case of layered antiferromagnetism (LAF) along the [001] direction. Obviously, the (001) surface, as one of these alternating planes, should be ferromagnetic (see Fig. 1). What is peculiar about the (001) surface is not its ferromagnetism but (i) the size of the magnetic moments, which are predicted to be enhanced by as much as $\sim\underline{300}\%$ with respect to the bulk value[1,3–5] and (ii) the predicted persistence of long-range order up to ~800 K (Refs. 5-7), i.e., well above the bulk Néel temperature of 312 K.

While the theoretical expectations have reached a wide consensus,[1,3–7] experimental results are partly at odds with those theoretical predictions. Two crucial experiments—both performed on the "clean" $p(1\times1)$ surface[8]—are the spin-resolved photoemission experiment by Meier, Pescia, and Schrieber[9,10] (SRPES) and the (non-spin-resolved) angle- and energy-resolved photoemission experiment (ARPES) by Klebanoff and coworkers.[11,12] In SRPES, which measures the net magnetization M within the first 2–3 layers, no magnetization was detected. In ARPES—which does not detect M directly—two surface states observed in the energy distribution curve of normally photoemitted electrons are interpreted as spin-split states, as expected from a ferromagnetically ordered surface. Clearly, the simple model of a ferromagnetic perfectly flat (001) surface, as assumed in calculations so far, cannot explain both these findings.

In this paper, we propose two different models of *antiferromagnetic order* on the Cr(001) surface to reconcile the experimental evidence with theoretical predictions. In model 1 we assume an inside-the-surface $c(2\times2)$ antiferromagnetic order with a transition to the bulk $p(1\times1)$ LAF structure (see Fig. 2). This spin configuration, never considered before, can no longer be ignored in favor of ferromagnetic order, in view of the recent discovery that Cr overlayers on Pd,[13] Au,[14] and Ag (Ref. 15) assume this spin configuration. In the framework of model 1, the zero magnetization in SRPES is the result of the cancellation of the sublattice magnetizations, while the surface states of ARPES arise from an *antiferromagnetic* exchange splitting. In model 2, we assume antiferromagnetic coupling between adjacent terraces consisting of ferromagnetic (001) planes (see Fig. 3) separated by single

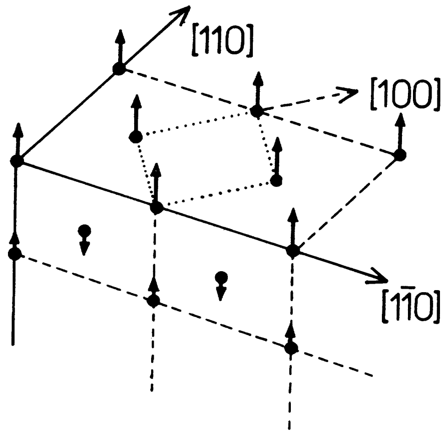

FIG. 1 The conventional layered antiferromagnetic structure. Spins are depicted perpendicularly to the surface only for graphical simplicity. The surface $p(1\times1)$ unit cell is given by dotted lines. Bulk moments are represented by shorter arrows than surface moments to signify their different size.

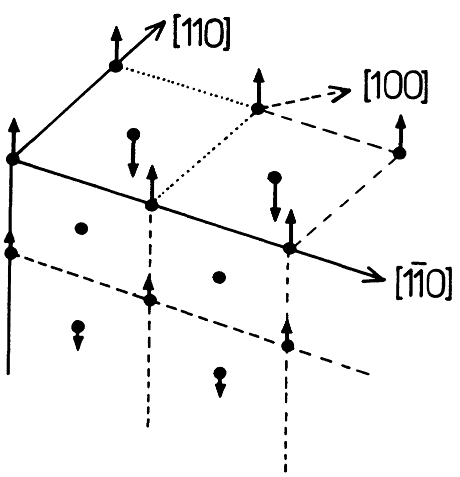

FIG. 2. The structure with the surface spins ordered in a $c(2\times2)$ AF structure and "frustrated" spins beneath. The $c(2\times2)$ unit cell is also given.

steps. Theoretical models usually assume perfectly flat surfaces. In practice, however, terraces separated mostly by single steps cannot be avoided.[16] The origin of terraces is twofold: At any finite temperature random terraces are likely to occur to minimize the surface free energy by maximizing the surface configurational entropy. Terraces with regular orientation arise from cutting (or polishing) the crystal slightly off the orientation of the low-index plane. Instead of creating an high-index plane with high-surface free energy, energy is released by forming regular terraces of low-index planes. The width of the terraces depends on the experimental preparation. For the Pt(111) surface, one of the microscopically flattest metal surfaces known, terrace width is certainly smaller than 1 μm.[17] In most cases, much less is achieved.[16] In model 2, the zero magnetization in SRPES arises from cancellation between oppositely magnetized terraces within the diameter of the light spot (~5 mm, i.e., much larger than the width of a single terrace), and the split states in ARPES are majority and minority states inside each ferromagnetic terrace.[18] The two models introduced differ in the length scale of their antiferromagnetic coupling—an atomic one in model 1 and a mesoscopic one in model 2. Applied to these two models, our calculations show that the $c(2\times2)$ spin configuration is energetically unfavorable with respect to the ferromagnetic one, leaving the topological antiferromagnetism as a "natural" explanation of experimental results.

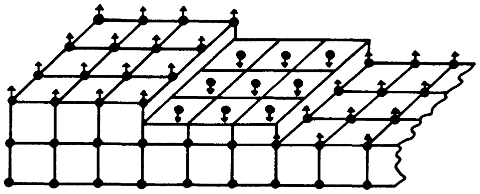

FIG. 3. Topological antiferromagnetic order of a Cr(001) surface with terraces separated by single surface steps. Different terraces are magnetized in opposite directions. Only surface spins are indicated.

In our line of reasoning, the first step is to compare the total energies of the paramagnetic (PM), ferromagnetic (FM), and $c(2\times2)$ antiferromagnetic (AF) surface. This can be done exactly with the use of a full-potential linearized argumented-plane-wave method.[19] We consider a three-layer Cr(001) slab in the paramagnetic, $p(1\times1)$ layered antiferromagnetic (see Fig. 1), and $c(2\times2)$ antiferromagnetic structure (see Fig. 2). For a comparison, we calculated also the isolated Cr(001) layer paramagnetically, $p(1\times1)$ ferromagnetically, and $c(2\times2)$ antiferromagnetically. As lattice constants we have chosen the chromium bulk lattice constant after Moruzzi, Janak, and Williams.[20] The calculations are performed within the framework of density-functional theory[21,22] applying the local-density approximation. The total energy differences between the magnetic structures and the local surface moments are collected in Table I, together with the results obtained for Cr on the (001) surfaces of Pd,[13] Ag,[15] and Au.[14] Our calculations show that for all systems mentioned above both magnetic configurations [$p(1\times1)$ FM and $c(2\times2)$ AF] exist, i.e., neither can *a priori* be ignored as possible spin configuration for the (001) surface of Cr. For all monolayer and overlayer systems the $c(2\times2)$ antiferromagnetic order on the surface has the lowest energy. In contrast, for the three-layer chromium film the layered antiferromagnetic structure with ferromagnetic (001) planes wins by about 0.16 eV/Cr atom. We are, therefore, left with the ferromagnetic surface having the lowest energy and SRPES detecting no net magnetization.

The next step is the introduction of a stepped surface with AF coupling between the terraces; see Fig. 3. A state-of-the-art calculation of the total energy of such a

TABLE I. Local magnetic moments M (in μ_B) within the muffin-tin sphere of the Cr surface atom as well as energy differences ΔE (in mRy) per unit cell and Cr atom for ferromagnetic (FM) and antiferromagnetic (AF) states of various Cr films. L denotes layer and PM denotes paramagnetic results.

	Local moments		Energy		
Cr systems	M_{FM}	M_{AF}	$E_{\mathrm{PM}}-E_{\mathrm{FM}}$	$E_{\mathrm{PM}}-E_{\mathrm{AF}}$	$E_{\mathrm{FM}}-E_{\mathrm{AF}}$
1L Cr(001)	4.40	3.91	−91.88	−121.69	−29.81
1L Cr on Pd(001) (Ref. 13)	3.87	3.45			−24.4
1L Cr on Ag(001) (Ref. 15)	3.78	3.57	−66.63	−85.77	−19.14
1L Cr on Au(001) (Ref. 14)	3.70	3.48	−57.35	−83.09	−25.74
3L Cr(001)	2.74	1.55	−14.82	−3.09	+11.73

system is out of the range of nowadays supercomputers. The existence of steps and terraces is experimentally undisputable: The layered antiferromagnetic structure of bulk Cr means that terraces separated by single steps are antiferromagnetically ordered provided steps do not perturb this "bulk-induced" topological AF order. On the basis of our experience on the various Cr-based systems summarized in Table I we are able to exclude a perturbation of the antiferromagnetism by steps. From the results of Table I we notice that in all systems the nearest-neighbor Cr atoms couple antiferromagnetically and the next-nearest-neighbors ferromagnetically. For the monolayer and overlayer systems, the nearest-neighbor Cr atoms are located in-plane leading to the $c(2\times2)$ AF structure, whereas for the Cr surface the nearest-neighbor atoms are atoms of adjacent (001) planes leading to a $p(1\times1)$ LAF structure. This suggests an *environmental insensitiveness* of magnetic coupling of the nearest-neighbor Cr atoms, which is also corroborated by the antiferromagnetic coupling of Cr dimers in Cu, Pd, and Ag.[23,24] This environmental insensitivity should ensure that in addition to the bulk-induced AF tendency also the local interaction between neighboring atoms on different sides of a single step is antiferromagnetic. Therefore, terraces consisting of single (001) planes separated by a single step will order antiferromagnetically.

Topological antiferromagnetism, which can be generally induced by virtually any deviation from a perfectly flat surface, is a simple way of reconciling theoretical predictions, spin-polarized results, and non-spin-polarized photoemission. The newly developed generation of high-resolution spin-polarized secondary-electron scanning microscopes[25] is *the* ideal tool to confirm this most obvious picture. Also spin-polarized energy resolved experiments, which are now feasible at synchrotrons, are necessary to corroborate with unambiguous experimental evidence the interpretations of non-spin-resolved spectroscopies. Even if our predictions about the type of magnetic order of a "realistic" Cr surface turn out to be true, that most elusive 300% enhancement of the magnetic moment, which represents the actual core of the theoretical predictions, still awaits experimental confirmation.

The calculations were performed using the full-potential linear argumented-plane-wave program for thin films. We would like to thank M. Weinert for interesting discussions. Part of this work was performed at the Institute for Solid State Physics, University of Tokyo. The computations were carried out on Cray X-MP computers in part under the auspices of the Höchstleistungsrechenzentrum (HLRZ) and the KFA Jülich.

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