

1D Lattice Distortions as the Origin of the $(2 \times 2)p4gm$ Reconstruction in γ' -Fe₄N(100): A Magnetism-Induced Surface Reconstruction

J. M. Gallego,¹ D. O. Boerma,² R. Miranda,² and Felix Ynduráin²

¹*Instituto de Ciencia de Materiales de Madrid-CSIC, Cantoblanco, 28049-Madrid, Spain*

²*Departamento de Física de la Materia Condensada and Instituto de Ciencia de Materiales Nicolas Cabrera, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain*

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The (100) surface of magnetic γ' -Fe₄N films epitaxially grown on Cu(100) shows a $(2 \times 2)p4gm$ reconstruction. The atom positions determined experimentally are properly accounted for by first-principles total energy calculations, which further reveal that the $(2 \times 2)p4gm$ reconstruction requires the topmost Fe₄N₂ plane to be magnetic and effectively decoupled from the rest of the crystal and that it originates from the perpendicular crossing of one-dimensionally dimerized Fe chains.

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Surface reconstructions have been the focus of intense research for more than 30 years [1,2]. They influence surface reactivity, determine kinetic pathways, and control electronic charge and spin transport across interfaces. It is generally accepted that they are energetically driven by reducing the density of dangling bonds in semiconductors or by maximizing the surface density in many clean metal surfaces [3]. However, the driving forces of many surface reconstructions have not been identified yet.

One of the oldest examples of reconstruction of a fcc (100) metal surface is the $(2 \times 2)p4gm$ or “clock” reconstruction [4] observed on different systems, such as light adsorbate layers [C/Ni(100) [4,5] or O/Rh(100) [6]], 2D surface alloys [e.g., Pd/Cu(100) [7]], or ultrathin Fe films grown on Cu(100) [8]. Here we report, both from the experimental and the theoretical point of views, on the physical origin of the $(2 \times 2)p4gm$ reconstruction observed in epitaxial films of γ' -Fe₄N(100), which has a driving force different from those previously reported in other systems. We find that 1D pairing of Fe atoms at the surface, in a mechanism similar to the Peierls distortion (but involving only minority spin electrons), lies behind the reconstruction driving mechanism. The instability is inherent to the corresponding 2D magnetic system. The required decoupling of the magnetic surface from the bulk is provided by additional N at the subsurface layer.

The experiments were performed in an ultrahigh vacuum (UHV) chamber (base pressure = 2×10^{-10} mbar) equipped with a scanning tunneling microscope (STM), a rear view low energy electron diffraction (LEED) optics, also used for auger electron spectroscopy (AES) [9], and a radio-frequency (rf) plasma discharge source [10]. Low energy ion scattering (LEIS) has been carried out in a separate UHV system with similar facilities for *in situ* growth and characterization [11]. All measurements reported here were performed at 300 K. The experimental results were compared with first-principles, theoretical calculations performed in the context of density functional

theory [12] using the SIESTA [13] method. For the exchange correlation potential we adopt a generalized gradients approximation [14]. The norm conserving pseudopotentials used follow the Troullier-Martins scheme [15] in the non-local form proposed by Kleinman and Bylander [16] and with partial core corrections.

Films of iron nitride up to a thickness of 200 ML were grown on Cu(100) by exposing the substrate at 700 K to a flux of atomic N from the rf source *and* a flux of Fe from an electron gun evaporator. This results in the growth of single-crystal, epitaxial films of γ' -Fe₄N(100) [11], as deduced from x-ray diffraction, conversion emission Mössbauer spectroscopy, magneto-optic Kerr effect, and Rutherford backscattering analysis [9]. The films are ferromagnetic below 760 K.

As shown in the inset of Fig. 1, the Fe atoms in γ' -Fe₄N form a fcc sublattice, with a N atom occupying the center

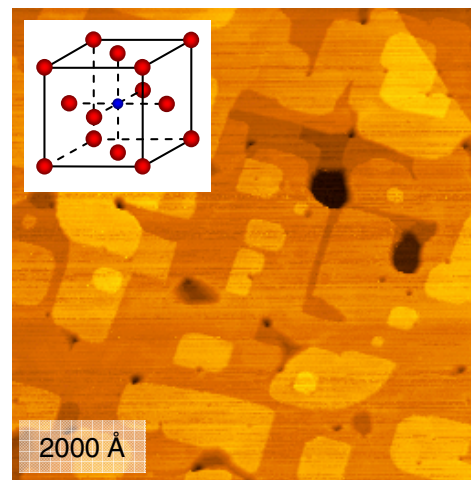


FIG. 1 (color online). Representative, 2000 Å × 2000 Å STM image of the surface of a γ' -Fe₄N(100) film. The inset shows the crystalline structure of Fe₄N with the Fe atoms represented as large (red) spheres and the N atoms as small (blue) spheres.

of the cube. Our total energy calculations give an equilibrium lattice parameter of $a_{\gamma'} = 3.82 \text{ \AA}$, within 0.7% of the experimental value $a_{\gamma'} = 3.79 \text{ \AA}$. The calculated magnetic moments of the two different Fe atoms are $2.99\mu_B$ and $2.29\mu_B$, to be compared with the experimental values $2.98\mu_B$ and $2.01\mu_B$, respectively. The cubic crystalline structure of γ' -Fe₄N along the (100) direction consists in alternate layers of Fe₄N₂ and Fe₄, both of square symmetry. Although the γ' -Fe₄N(100) surface could then have two types of terminations, our LEIS data (see below) indicate that the surface is chemically homogeneous. Furthermore, the surface morphology of these single-crystal epitaxial films, as shown in Fig. 1, displays atomically flat and electronically homogeneous terraces separated by monoatomic, 1.9 \AA -high, steps. Our first-principles calculations indicate that the Fe₄N₂ termination is 1.5 eV per surface unit cell lower in energy than the Fe₄ one. This, together with the strong affinity for N of any hypothetical Fe terrace [17], leads to the observed single surface termination consisting in Fe₄N₂ terraces separated by monoatomic steps.

The expected LEED pattern for the Fe₄N(100) unreconstructed surface would show a $c(2 \times 2)$ symmetry with respect to the Cu(100) substrate. Samples prepared at standard deposition rates of Fe show indeed the LEED and STM pattern expected for a nonreconstructed surface. Samples grown in excess N, however, show a surface reconstruction identified by a $(2 \times 2)p4gm$ LEED pattern (inset of Fig. 2). AES data systematically show a larger amount of N on the surface region for the $(2 \times 2)p4gm$ reconstructed surfaces. On the other hand, LEIS measurements indicate that the N/Fe atomic ratio at the external surface is approximately the same for both reconstructions.

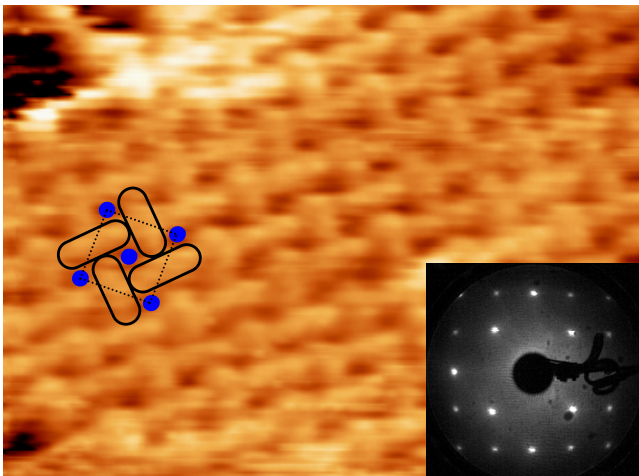


FIG. 2 (color online). Atomically resolved STM image of the $(2 \times 2)p4gm$ reconstruction of γ' -Fe₄N(100) recorded with sample bias voltage of +0.3 V and tunneling current of 1.2 nA. The unit cell is indicated by the dotted line and the inset reproduces the LEED pattern corresponding to this surface ($E_p = 110 \text{ eV}$).

The $p4gm$ superstructure is characterized by the absence of the four first half-order spots of the simple (2×2) LEED pattern. This indicates the existence of two perpendicular glide planes which produce the systematic extinction of the half-order spots along $\langle 110 \rangle$ directions. The STM image of Fig. 2 shows an atomic arrangement with a characteristic “weaving” pattern. The corresponding surface unit cell at the surface is identical to the one determined by LEED.

The atomic positions at the surface of a $(2 \times 2)p4gm$ reconstructed γ' -Fe₄N(100) film, have been determined by measuring the azimuthal dependence of the intensity of the Ar, Fe, and N peaks in LEIS measurements. The atomic positions for Fe and N were determined by comparing the measured LEIS spectra with simulations carried out with the code MATCH [18]. Figure 3 shows the experimental data and the best fit, which gives lateral displacements of the Fe atoms along $\langle 110 \rangle$ of $0.43 \pm 0.05 \text{ \AA}$. The N atoms reside on fourfold hollow sites $0.27 \pm 0.05 \text{ \AA}$ above the Fe plane. The resulting surface arrangement can be visualized as if the square units of four Fe atoms around a N atom would rotate alternatively clockwise and counterclockwise around the surface normal, or else as if the Fe atoms would dimerize in two perpendicular directions, as schematically shown in Fig. 4.

In order to understand the nature of the reconstruction and its driving force we choose, as a first model system, an isolated 2D layer of Fe₄N₂(100). Its calculated equilibrium

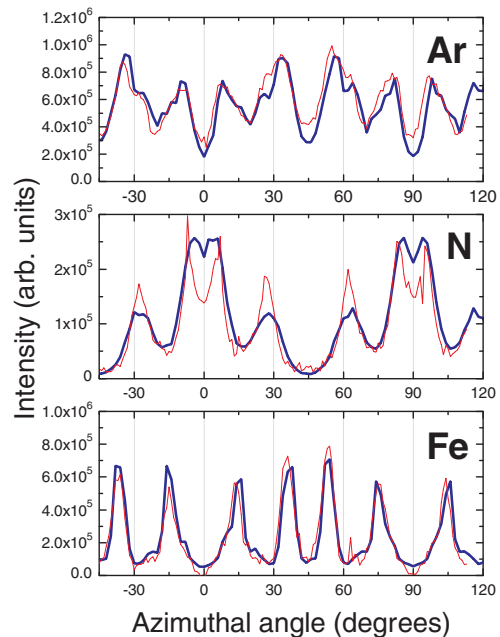


FIG. 3 (color online). Azimuthal dependence of the intensity of low energy ion scattering peaks measured with a time of flight technique and corresponding to Ar, N, and Fe recorded on the $(2 \times 2)p4gm$ Fe₄N(100) surface. The experimental data are shown as a thin line (in red), while the thick (blue) line shows the corresponding best fit. The zero in the azimuthal angle corresponds to the $\langle 110 \rangle$ crystallographic direction.

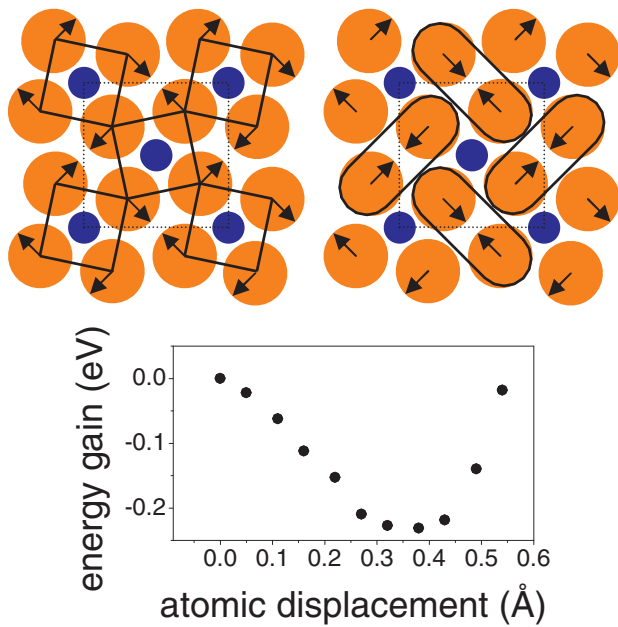


FIG. 4 (color online). Energy gain per unit cell of a 2D $\text{Fe}_4\text{N}_2(100)$ layer as a function of the lateral displacement of the Fe atoms, which leads to a $(2 \times 2)p4gm$ reconstruction. The starting configuration corresponds to the calculated equilibrium lattice parameter of bulk Fe_4N . The resulting atomic model for the $(2 \times 2)p4gm$ reconstructed surface is shown in the upper panels. The N atoms are shown as small (blue) spheres and the Fe atoms as large (red) spheres. The arrows indicate the direction of displacement of the Fe atoms. Notice that the lateral atomic displacements of Fe can be interpreted as rotated squares or else, as alternating dimers.

lattice parameter is $a_{\gamma'} = 3.65 \text{ \AA}$, i.e., the layer would be under substantial tensile strain when placed at the lattice parameter imposed by the bulk γ' - Fe_4N crystal. For the bulk lattice parameter (3.82 \AA), Fig. 4 shows that the total energy displays a well defined minimum as a function of the lateral displacements of the Fe atoms. The layer, thus, would spontaneously lower its symmetry giving rise to a $(2 \times 2)p4gm$ reconstruction. This is also true if the calculation is done at the 2D layer equilibrium lattice constant (3.65 \AA), which shows that strain in the layer is *not* responsible for the reconstruction. The predicted lateral displacement of the Fe atoms is $0.36 \pm 0.05 \text{ \AA}$. The corresponding energy gain is 220 meV per unit cell.

The ground state of this 2D Fe_4N_2 layer is ferromagnetic with a magnetic moment of $2.98\mu_B$ per Fe atom. Total energy calculations shown in Fig. 5(a) indicate that if the system is *not* allowed to be magnetic, the nonreconstructed layer is more stable. The $(2 \times 2)p4gm$ reconstruction is lower in energy only for magnetic moments above $2\mu_B$. Notice that the reduction in energy due to magnetism is of the order of 3 eV/unit cell, while the one due to the reconstruction amounts to 220 meV/unit cell. No antiferromagnetic order has been considered in the calculations.

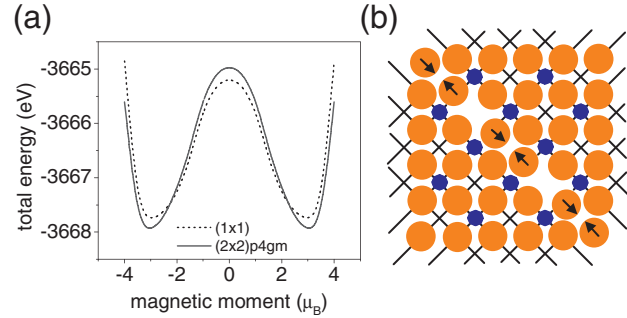


FIG. 5 (color online). The two main characteristics of the reconstruction, magnetism and 1D character, are illustrated by: (a) Calculated total energy per unit cell of a 2D $\text{Fe}_4\text{N}_2(100)$ layer as a function of the magnetic moment per Fe atom. (b) Atomic positions resulting from a calculation in which all the Fe atoms are fixed, except those along one particular row of a 2D $\text{Fe}_4\text{N}_2(100)$ layer. The Fe atoms (large, red, circles) dimerize to form pairs in a 1D lattice distortion. A superposition of the dimers causes the weaving pattern seen in STM images of the $(2 \times 2)p4gm$ reconstruction.

The behavior of a bulk crystal was simulated by carrying out first-principle calculations of the ground state structure for slabs of different thicknesses until the forces were below 0.02 eV/\AA . For slabs with the ideal bulk composition, no reconstruction has been retrieved, independently of whether the slab was terminated with a Fe_4N_2 layer or with a Fe_4 layer covered with adsorbed N [17].

One possibility of getting the reconstruction on a bulk-terminated slab is by saturating the subsurface layer with N, i.e., by placing a Fe_4N_4 layer underneath the Fe_4N_2 surface. In this case the surface displays a clear energetic preference for the $(2 \times 2)p4gm$ reconstruction, with a lateral displacements of the Fe atoms of $0.30\text{--}0.45 \text{ \AA}$ in agreement with the 2D Fe_4N_2 layer calculation of Fig. 4, and a vertical N-Fe distance around 0.2 \AA . The subsurface layer shows an important buckling of about 0.7 \AA . Table I shows the atomic coordinates of Fe and N in the first two layers. Atoms in layers below occupy essentially their bulk positions. The predicted displacements of the surface atoms are in good agreement with the fit to the LEIS data. Notice that, for this structure, while the amount of N at the outer surface would be the same for the reconstructed and the unreconstructed surfaces (in agreement with LEIS), the total amount of N detected in the first few layers would be larger for the reconstructed than for the bulklike surface (as determined by AES data). The Fe_4N_4 subsurface layer effectively decouples the surface from the bulk and, thus, the surface behaves similarly to the 2D self-standing Fe_4N_2 layer described above.

Different physical mechanisms have been invoked in the literature as the driving force behind the $p4gm$ reconstructions. For adsorbates, such as C [4] or N on Ni(100) [19], it has been proposed that the formation of a fifth bond with substrate atoms in the subsurface layer sinks the small atoms into the surface, which then relaxes the resulting

TABLE I. Atomic coordinates, x , y , and z of Fe and N in the first two atomic layers of a thick Fe_4N slab. The coordinates of all the atoms in the other layers are found at the bulk positions. The displacements reported in the last three columns are given with respect to the bulk positions. Notice the relaxation and buckling of the first two layers.

	x (Å)	y (Å)	z (Å)	Δx (Å)	Δy (Å)	Δz (Å)
N	0.000	0.000	6.511	0.00	0.00	0.78
N	2.702	2.709	6.511	0.00	0.00	0.78
Fe	1.672	1.032	6.296	-0.32	0.32	0.57
Fe	1.142	-1.553	6.286	0.21	0.20	0.56
Fe	-1.151	1.562	6.286	-0.20	-0.21	0.56
Fe	-1.681	-1.023	6.306	0.33	-0.33	0.58
Fe	-0.005	-0.002	4.562	0.01	0.00	0.74
Fe	2.705	2.710	4.561	0.00	-0.01	0.74
Fe	2.705	0.000	3.806	0.00	0.00	-0.01
Fe	0.001	2.704	3.803	0.00	0.00	-0.02
N	1.362	1.342	4.042	-0.01	0.01	0.22
N	1.340	-1.362	4.033	0.01	0.01	0.21
N	-1.342	1.364	4.035	-0.01	-0.01	0.22
N	-1.360	-1.344	4.015	0.01	-0.01	0.20

compressive surface stress by means of the $p4gm$ reconstruction [20]. For surface alloys, the presence of a corrugated second layer has been pointed out as essential [7]. First-principles calculations, however, indicate that isolated metal layers with square symmetry are inherently unstable (although with an energy barrier) towards this atomic rearrangement [21].

The physical nature of the $p4gm$ reconstruction described here is *not* similar to the ones reported previously. In the present case the surface needs to be magnetic and decoupled from the bulk, and the driving force is a dimerization of the Fe atoms in two mutually perpendicular directions. Figure 5(b) shows the calculated atomic positions for a 2D $\text{Fe}_4\text{N}_2(100)$ layer with all the Fe and N atoms *fixed*, except those along one particular $\langle 011 \rangle$ row. The calculated minimum of energy occurs when the Fe atoms form pairs. The arrows indicate the direction and extent (of the order of 0.4 Å) of the displacement. Our calculations indicate that this dimerization is the result of a 1D distortion of the lattice that reduces the minority spin density of states at the vicinity of the Fermi level. The majority spin band lies well below the Fermi energy. When all the atoms are allowed to move, pairing occurs in two mutually perpendicular directions, resulting in dimers of alternate orientation whose superposition gives rise to the weaving pattern seen in STM images of this $(2 \times 2)p4gm$ reconstruction.

In summary, the surface reconstruction of $\text{Fe}_4\text{N}_2(100)$ observed, although of the same $p4gm$ symmetry that some others previously described, is of a rather different origin: (i) it requires the surface to be magnetic; (ii) it requires the surface to be effectively decoupled from the rest of the crystal, which can be achieved by saturating the subsurface

layer with additional N; and (iii) it involves two 1D pairings of Fe atoms perpendicular to each other.

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