

EXPERIMENTAL REPORT RAPPORT D'EXPERIENCE

Programme Committee Proposal Number
N° Projet Comité de Programme

32 03 72

PROJECT TITLE : *TITRE DU PROJET* :

c(2x2) Mn/Ni(110) surface structure.

LIGNE : **BM32 (CRG-IF) – SUV**

NUMBER OF RUNS USED: **21**

STARTING DATE **31/08/2002**

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The aim of this project was to solve the surface structure obtained by deposition of Mn on Ni(110). A c(2x2) superstructure has been observed few years ago after deposition of about 0.5 monolayers (ML) of Mn at room temperature.ⁱ This Ni(110)-c(2x2)Mn reconstruction seems to belong to a class of magnetic surface alloys, having for prototype the Cu(100)-c(2x2)Mnⁱⁱ surface and including also Cu(110)-c(2x2)Mnⁱⁱⁱ and Ni(100)-c(2x2)Mn.^{iv} In these alloys the Mn occupies substitutional sites at the surface following a chessboard arrangement. A large rippling is observed with Mn atoms shifted outward by 0.2-0.3 Å. *Ab initio* calculations for the Cu(100)-c(2x2)Mn phase concluded that this rippling is associated with an high spin state for Mn (3.75 μ_B per atom), while a paramagnetic surface should be almost flat.ⁱⁱ

X-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) at the Mn $L_{2,3}$ edge of Cu(100)-c(2x2)Mn and Ni(100)-c(2x2)Mn showed that, in both cases, Mn is in a high spin ground state, confirming the theoretical predictions.^v

As first step, the growing conditions were optimized following the surface evolution first by RHEED, and then by surface x-ray diffraction (XRD). By measuring the scattering intensity during deposition at a well-defined point ($L=1.6$) of the (1/2 1/2) fractional rod both the coverage and the temperature were refined to obtain the best c(2x2) superstructure. The quantitative analysis of the XRD data showed that the saturation coverage is about 0.5 Mn ML, while the most suited temperature

is 440 K. At this temperature the surface is quite flat, as assessed by the shape of the crystal truncation rods (CTR) close to antiphase conditions, and the c(2x2) domains are relatively large, as deduced from the width of the non integer rods (an isotropic Gaussian model gives correlation lengths of 17.3 nm and 3.3 nm at 440 K and room temperature respectively).

We find that the onset of the c(2x2) occurs around $\Theta \sim 0.35$ ML whatever the temperature in the range explored. In the case of Mn/Cu(100), STM^{vi} showed a strong enhancement in the mobility around 0.3 Mn ML, which was correlated to the ordering process into the c(2x2) structure. This was explained with a repulsive interaction between Mn atoms on nearest-neighbor sites.

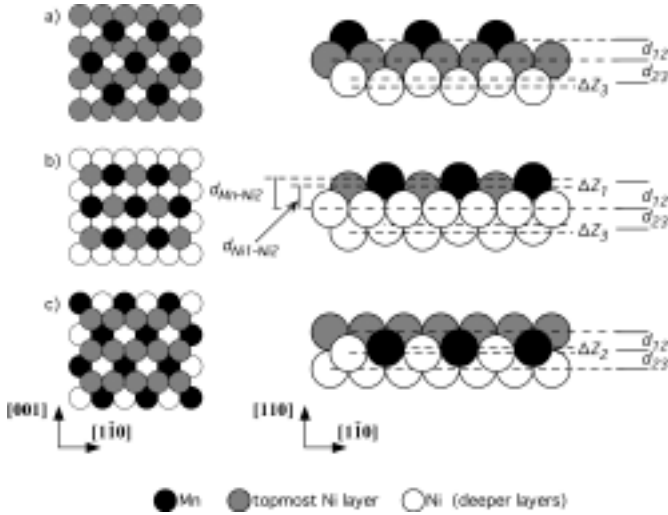
Once optimized the c(2x2) structure, we collected data for quantitative analysis.

A grazing incidence angle of 0.18° was used, to increase the signal-to-noise ratio (the critical angle for total reflection is 0.19°), since quite weak fractional spot were expected. For this reason, special care was taken in recording equivalent rods. We measured the (10), (01), (11), (1/2 1/2), (1/2 3/2), (3/2 1/2) rods and all their respective equivalents in the p2mm symmetry, that is a total of 310 reflections distributed along 20 rods. They were reduced to 100 non-equivalent reflections by averaging, with a good agreement between equivalent ones ($\epsilon=0.032$). A photon energy of 18 KeV was employed, allowing for a large L range.

Three main structural models were considered (Fig.1):

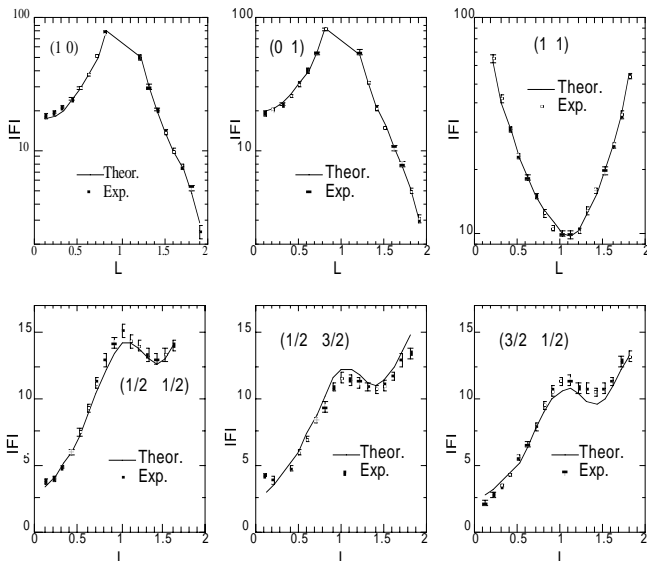
a) a pure Mn c(2x2) overlayer;

b) a perfectly ordered Mn-Ni surface alloy;
c) a perfectly ordered Mn-Ni underlayer.



For each of them, a Ni(110) substrate with possibly modified interlayer spacings was assumed. The data analysis showed that neither the overlayer model nor the alloy underlayer fit the experiment as assessed by enormous values of χ^2 , 200 and 50 respectively, for meaningful values of the Debye factors.

In contrast, a surface alloy confined to the top layer (model b) fits very well the experimental data ($\chi^2 = 3.7$). Using this model, we have optimized three interlayer spacings (d_{12} , d_{23} , and d_{34}), the relative vertical displacement of the two species presents in the top layer (buckling ΔZ_1), and the possible buckling of the third layer (ΔZ_3). The interlayer spacing d_{ij} refers to the mean position, when the layer includes two sites (see Fig. 1). The best fit is shown in Fig.2.



The agreement is slightly improved by considering a small fraction (7%) of adatoms on

the fourfold site ($\chi^2 = 2.6$, R -factor=0.028). In Table I, the results are compared with Cu(110)-c(2x2)Mn.

	Ni(110)- c(2x2)Mn	Cu(110)-c (LEED, re)
ΔZ_1 [Å]	0.30±0.01	0.22±0.0
ΔZ_3 [Å]	0.036±0.005	0.01±0.0
d_{12} [Å]	1.28±0.01	1.31±0.0
d_{23} [Å]	1.254±0.005	1.29±0.0
d_{34} [Å]	1.243±0.005	1.27±0.0
d_b [Å]	1.246	1.278
ML _{adatoms}	0.07±0.01	
B_1 [Å ²]	0.70±0.08	
B_2, B_3 [Å ²]	0.35	

The main feature is the large corrugation of the top layer. Indeed, Mn atoms reside 0.30 above the Ni sublattice. The presence of Mn atoms in the top layer has also some influence on the third layer corrugation: Ni atoms located below the Mn sites are shifted outward by 0.035 compared to the second sublattice. The fit is very sensitive to this parameter, which is fully responsible for the local minima around $L=1.5$ in the non-integer rods.

In bulk $MnNi_3$ (AuCu₃ structure type), the Mn has twelve Ni nearest-neighbors at $D_{Mn-Ni} = 2.54$. In the surface alloy, the corresponding distance $\langle D_{Mn-Ni} \rangle = 2.58$ - calculated with the first shell of atoms (two at 2.51, four at 2.59, and one at 2.67) - is significantly larger, which means a bigger volume for the Mn adsorbate. The large buckling is without any doubt the sign of huge magnetovolume effects and a large magnetic moment on the Mn site is expected.^{vii}

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