PHYSICAL REVIEW B, VOLUME 65, 233404

Tensor LEED analysis of the Ni(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb surface

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(Received 18 January 2002; published 29 May 2002)

The structure of the Ni(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb surface has been determined by quantitative low-energy electron diffraction (LEED), using multiple-scattering simulations of the measured diffracted beam intensities with a tensor-LEED program. The results confirm that the surface comprises a single-layer substitutional alloy of stoichiometry Ni_2Pb (with all atoms in ‘‘fcc’’ sites relative to the underlying Ni) and clearly excludes a surface/subsurface stacking fault (with occupation of ‘‘hcp’’ sites) like that found for similar phases of Sb on Cu(111) and Ag(111). Within the surface alloy layer the Pb atoms are 0.73 ± 0.05-Å higher above the surface than the surrounding Ni atoms in the alloy layer. This magnitude of rumpling is in excellent agreement with a recent medium-energy ion scattering investigation of this surface, but is significantly larger than that of an earlier low-energy ion scattering investigation. Compared to the rumpling amplitude of 1.67 Å expected from a simple hard-sphere model based on bulk metallic radii, however, it confirms a strong reduction of the effective atomic radii in this surface alloy.

DOI: 10.1103/PhysRevB.65.233404 PACS number(s): 68.35.Ct, 68.43.Fg, 68.47.De, 61.14.Hg

There are now many examples of the observation that the deposition on metal surfaces of atoms in the submonolayer coverage range can lead to these adsorbate atoms occupying substitutional sites in the outermost atomic layer to produce a single-layer surface alloy.[1] This can even occur for some adsorbate/substrate element combinations immiscible in the bulk, reflecting the different energetics of the surface. One question that has attracted some interest in these systems is what the role of effective atomic radii of the adsorbate atoms is in these surface alloys, which determines the degree of ‘‘rumpling’’ of the alloy layer. If the deposited atoms have larger atomic radii than that of the substrate atoms they replace, then because the periodicity of the surface alloy parallel to the surface is fixed at the value of the underlying substrate (i.e., the surface alloy layer is pseudomorphic), a simple hard-sphere picture would predict that the adsorbate atoms would have a larger layer spacing relative to the underlying second layer of the substrate than that of the undisplaced outer-layer substrate atoms. This simply reflects the inability of a larger atom to be fully accommodated in the vacant site produced by the removal of a smaller substrate atom from the surface layer. Recent quantitative structure determinations of quite a number of surface alloy phases, however, indicate that the rumpling observed is almost always less than that predicted by this simple hard-sphere model, and this has been suggested to be a consequence of the valence electron depletion in the surface layer due to spillover into the vacuum, allowing the surface-layer atoms to approach one another more closely than in a bulk solid.[2]

One system for which this effect appears to be especially large is the Ni(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb surface formed by 0.33 ML of Pb on Ni(111). A structural investigation of this surface was made by low-energy ion scattering[3] and reached the conclusions that the Pb atoms did occupy substitutional sites as opposed to overlayer sites, and that the surface alloy rumpling had an amplitude of 0.2 Å, with the Pb atoms higher above the underlying substrate. The authors of this paper made no comment on this value, which, as shown below, is surprisingly small. A more recent medium-energy ion scattering (MEIS) study,[4] using 100-keV H^+ incident ions, explored as possible structural models not only substitutional and overlayer adsorption sites, but also a surface alloy layer in which all atoms occupy the ‘‘hcp’’ hollow sites, directly above second-layer Ni atoms in the underlying substrate, rather than the usual ‘‘fcc’’ hollows above third-layer substrate Ni atoms. This surface stacking fault model had previously been found to be the correct structural model for Ag(111)$(\sqrt{3}\times\sqrt{3})R30°$-Sb and Cu(111)$(\sqrt{3}\times\sqrt{3})R30°$-Sb.[5–7] The MEIS investigation of Ni(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb showed that this surface is *not* faulted in this way, and while the overall analysis did not formally distinguish the simple (unfaulted) surface alloy layer from a model involving 0.33 ML of Pb on fcc overlayer sites, the subset of data most sensitive to this difference did favor the surface alloy model. For this substitutional alloy model the amplitude of rumpling, with the Pb atoms higher above the underlying substrate, was found to be 0.65 ±0.15 Å.

In their bulk elemental forms the effective radii of Ni and Pb (i.e., half the value of the nearest-neighbor interatomic distances) are substantially different, 1.25 for Ni and 1.75 Å for Pb. A simple model based on touching hard spheres with these radii in which a Pb atom replaces a surface Ni atom predicts that the Pb atom would have a layer spacing relative to the underlying complete Ni layer, which is 1.67 Å, larger than that of the surrounding Ni atoms in the ‘‘same’’ alloy layer, almost as large as the (111) layer spacing of the Ni substrate (2.03 Å). Clearly, the two experimental values of this surface rumpling [0.20 (Ref. 3) and 0.65 Å (Ref. 4)] are very much smaller. One must conclude, therefore, that either the Ni_2Pb pseudomorphic surface alloy phase really does involve very much smaller effective atomic radii, or the two previous experimental determinations are fundamentally flawed. To resolve this question, and to try to establish which, if either, of the two rather different previous experimental values of the Pb layer spacing is correct, we present here the results of a structure determination of this surface using the technique of quantitative low-energy electron diffraction (LEED).

The experiments were performed using a standard ultrahigh-vacuum (UHV) chamber equipped with the usual range of facilities for sample preparation and surface characterization together with a computer-controlled LEED optic. The base pressure of the chamber was typically $(1-2)\times 10^{-10}$ torr. A Ni(111) crystal disc of approximately 12-mm diameter by 2-mm thickness from a single-crystal boule was initially prepared by x-ray Laue alignment (to within approximately 0.5°), spark erosion, and mechanical polishing prior to being placed in the UHV surface science chamber. The crystal was cleaned *in situ* by repeated cycles of bombardment with 1-keV Ar^+ ions and subsequent annealing to 650 °C until a clean and well-ordered surface was obtained as judged by x-ray photoelectron spectroscopy and qualitative LEED. The Ni(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb surface phase was prepared following the procedure originally reported by Umezawa and co-workers[3] and subsequently used in the previous MEIS study.[4] This involved depositing Pb from a Knudsen cell operating at a temperature of 600 °C onto the Ni(111) substrate to a nominal coverage of 0.45 ML. At the completion of this stage the initial (1×1) LEED pattern is transformed to a (3×3) LEED pattern. Annealing the crystal at 600 °C for several seconds and allowing the sample to cool to room temperature resulted in a sharp $(\sqrt{3}\times\sqrt{3})R30°$ diffraction pattern. In the earlier MEIS study[4] faint additional (3×3) diffracted beams were still present after this treatment, but in the present case there was no sign of this residual second phase in the LEED pattern. LEED diffracted beam intensities were measured using incident electron beam energies in the range 50 to 500 eV at room temperature, using an Omicron video-LEED system at nominal normal incidence. Careful checks, comparing the intensity-energy spectra of symmetry-equivalent diffracted beams, were undertaken to ensure that a geometry extremely close to normal incidence was achieved. Intensity-energy (I-E) spectra were collected for five integral order and two fractional order beams with a total-energy range of 1974 eV, and these were used in the subsequent structure analysis.

The structure determination was effected by the usual approach in LEED of simulating the diffracted beam I-E spectra for a range of model structures, comparing these with the experimental data with the aid of the Pendry R factor (reliability factor) R_P.[8] The LEED calculations were performed using the Barbieri/Van Hove symmetrized automated tensor LEED (SATLEED) computer codes with their associated programs to calculate the muffin-tin potential and scattering phase shifts.[9,10] Five different structural models were considered. Three of these were for a simple Pb overlayer with the Pb atoms occupying either the fcc hollow sites (directly above third-layer Ni atoms), the hcp hollow sites (directly above second-layer Ni atoms) or atop the outermost-layer Ni atoms. In addition, two possible substitutional surface alloy models were investigated: a simple alloy with all Ni and Pb atoms in fcc hollows relative to the underlying Ni substrate and a faulted alloy layer with all atoms in this layer in hcp hollows.

For the initial stage of optimizing each model, new sets of 10 scattering phase shifts were generated for each of the structures of interest, initially based on structures using touching hard spheres with the bulk metallic radii that defined the starting geometry for each model. The subtle changes in the scattering phase shifts arising from this approach are probably not important in all but the finest structural refinements, but this approach is essentially self-consistent. The atoms in the outermost three layers were allowed to move freely perpendicular to the surface, subject to the point-group symmetry. For example, this symmetry allows a rumpling of the outermost Ni layer for the model involving Pb atoms adsorbed in top sites, the Ni atoms directly below the Pb atoms having a different layer spacing, to the Ni atoms that are not covered in this way. In the case of the faulted alloy and hcp overlayer models, rumpling of the second complete Ni layers is allowed. Each of the three outermost layers (including the Ni_2Pb layer for the alloy models) was treated in the calculation as a composite layer with the multiple scattering being calculated by full matrix inversion. The rumpling of the Ni layers was actually found to have little effect on the R factor. Having established the approximate best-fit parameters values for each model, new optimizations were performed using 12 scattering phase shifts calculated for these revised starting parameters. The atomic vibrational amplitudes used initially for the Pb and Ni atoms were based on the bulk Debye temperatures of the respective bulk solids (105 and 450 K, respectively), but these were later adjusted in the final structural optimization stages.

The lowest values of the Pendry R factor (R_p) for each model obtained after these optimizations showed a very clear preference for the (unfaulted) substitutional alloy model with a value of 0.14. The lowest R-factor values for the other models were 0.38 (top overlayer), 0.39 (fcc overlayer), 0.42 (hcp overlayer), and 0.47 (faulted alloy layer). All these values are far outside the variance of the lowest value for the unfaulted alloy and the associated structures can clearly be excluded. For this preferred model a final stage of structural optimization was conducted, adjusting the effective vibrational amplitudes of the Ni and Pb atoms in the alloy surface

TABLE I. Comparison of structural parameter values for the unfaulted surface alloy model of the Ni(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb surface derived from the current LEED study and the previous MEIS study (Ref. 4) z_{Pb} is the layer spacing of the Pb atoms relative to the outermost complete Ni layer. z_{12} is the layer spacing of the Ni atoms in the same alloy layer to the first compete Ni layer. z_{23} and z_{34} refer to the first to second and second to third complete Ni layer spacings, respectively. The asterisks indicate that bulk values were assumed for these parameters.

Parameter (Å)	LEED	MEIS
z_{Pb}	2.73 ± 0.05	2.64 ± 0.14
z_{12}	2.00 ± 0.01	1.99 ± 0.05
z_{23}	2.04 ± 0.02	2.03*
z_{34}	2.00 ± 0.02	2.03*

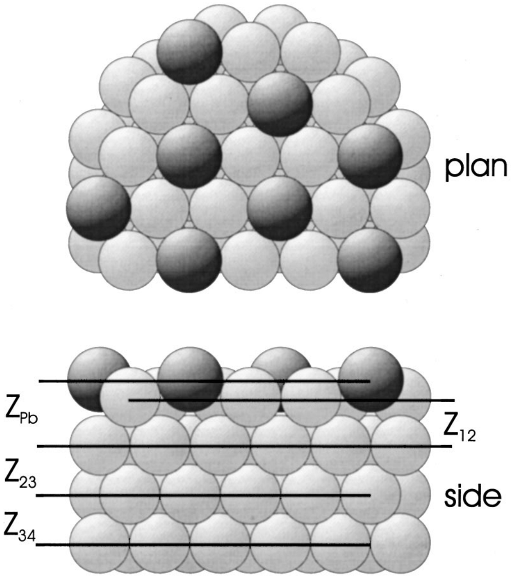

FIG. 1. Plan and side views of a schematic model of the substitutional surface alloy model of the Ni(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb surface showing the definition of the principal structural parameters. The dark shaded spheres represent the Pb atoms, which have been drawn with a radius appropriate to give a touching hard-sphere picture.

layer perpendicular to the surface. This led to a reduction of the R factor to 0.11; the optimum value of the vibrational amplitudes of the surface Ni atoms increased by a factor of 1.8 relative to the bulk value, but those of the Pb atoms (already much larger due to the use of the lower Pb Debye temperature) showed no such enhancement. This modification of the vibrational amplitudes, broadly consistent with expectations for a surface layer, produced no significant changes in the optimized structural parameters.

Table I shows the values of the optimized structural parameters for this model, while Fig. 1 shows a schematic model of the structure with these parameters defined, and Fig. 2 shows the comparison of the experimental and theoretical LEED I-E spectra for this structure. The quality of the fit is evidently good, both visually and as reflected by the value of 0.11 of the Pendry R factor. Table I also includes the structural parameter values obtained in the earlier MEIS study of this system.[4] The agreement is clearly good, with all parameters agreeing to better than the estimated precision of the (less precise) MEIS results. The amplitude of the rumpling of the surface alloy found in the LEED is 0.73 ± 0.05 Å, which is in good agreement with the MEIS value of 0.65 ± 0.15 Å. This value is also significantly larger that the 0.2 Å found in the earlier low-energy ion scattering study.[3] While this provides strong evidence that this smaller rumpling value is probably inaccurate, an even more significant conclusion that the LEED results give is that the rumpling amplitude is much less that the value of 1.67 Å predicted by a simple hard-sphere model based on bulk metallic radii. As such this confirms the earlier finding of a strong reduction in the effective radii, which may be attributed to the influence of surface valence electron charge smoothing and the associated surface stress effects.

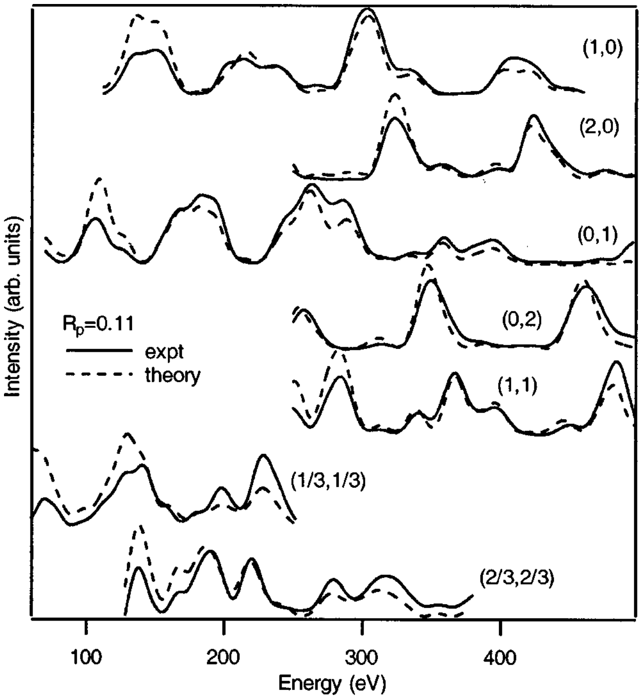

FIG. 2. Comparison of experimental LEED I-E spectra for the Ni(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb surface with the best-fit theoretical curves for the substitutional alloy model. The associated structural parameter values are given in Table I.

The authors are pleased to acknowledge the financial support of the European Commission under Grant No. CI1* CT94 0063 and of the Engineering and Physical Sciences Research Council. They would also like to thank Professor M. A. Van Hove and Dr. A. Barbieri for supplying the PHASE SHIFT and SATLEED software packages, and Dr. E. Soares for useful discussions.

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[1] *The Chemical Physics of Solid Surfaces, Alloy Surfaces and Surface Alloys*, edited by D. P. Woodruff (Elsevier, Amsterdam, 2002), Vol. 10.

[2] D. P. Woodruff, D. Brown, P. D. Quinn, T. C. Q. Noakes, and P. Bailey, Nucl. Instrum. Methods Phys. Res. B **183**, 128 (2001).

[3] K. Umezawa, S. Nakanishi, T. Yumura, W. M. Gibson, M. Watanabe, Y. Kido, S. Yamamoto, Y. Aoki, and H. Naramoto, Phys. Rev. B **56**, 10 585 (1997).

[4] D. Brown, P. D. Quinn, D. P. Woodruff, P. Bailey, and T. C. Q. Noakes, Phys. Rev. B **61**, 7706 (2000).

[5] S. A. de Vries, W. J. Huisman, P. Goedtkint, M. J. Zwanenburg, S. L. Bennett, I. K. Robinson, and E. Vlieg, Surf. Sci. **414**, 159 (1998).

[6] P. Bailey, T. C. Q. Noakes, and D. P. Woodruff, Surf. Sci. **426**, 358 (1999).

[7] E. A. Soares, C. Bitencourt, V. B. Nascimento, V. E. de Carvalho, C. M. C. de Castilho, C. F. McConville, A. V. de Carvalho, and D. P. Woodruff, Phys. Rev. B **61**, 13 983 (2000).

[8] J. B. Pendry, J. Phys. C **13**, 937 (1980).

[9] M. A. Van Hove, W. Moritz, H. Over, P. J. Rous, A. Wander, A. Barbieri, N. Materer, U. Starke, and G. A. Somorjai, Surf. Sci. Rep. **19**, 191 (1993).

[10] A. Barbieri and M. A. Van Hove (private communication).