Structure Determination of an Adsorbate-Induced Multilayer Reconstruction: (1×2)-H/Ni(110)

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The reconstructed (1×2) structure formed by saturation of a Ni(110) surface with adsorbed H atoms at $T < 180$ K was investigated by LEED. Excellent agreement between experimental and calculated I-V spectra for eleven nonequivalent beams was obtained for a model in which parallel rows of Ni atoms in the topmost layer are laterally shifted by 0.3 Å ("row pairing") and which exhibits periodic vertical displacements ("buckling") of the atoms in the second layer.

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Reconstruction phenomena on metal surfaces so far have been dealt with as confined to the topmost layer, in contrast to semiconductor surfaces where they are known to extend farther into the subsurface region.[1] Only recently LEED analyses of the clean, reconstructed (1×2) surfaces of Au(110)[2] and Ir(110)[3] revealed that also deeper layers may be distorted—a fact which is not accessible to investigation by techniques which essentially probe only the properties of the outermost atomic layers, such as He diffraction. In the present Letter we demonstrate this effect for the first time also for an adsorbate-induced reconstruction, the (1×2)H reconstruction on Ni(110). Ending a longstanding controversy, it is also unambiguously established that this reconstruction belongs to the "row pairing" type, in contrast to the "missing row" type reconstruction of the clean (110) surfaces of Au, Ir, and Pt.[1] It is felt that these results are of general importance for a detailed understanding of the interaction between chemisorbed particles and metal surfaces.

Exposure of a clean Ni(110) surface to H_2 below 180 K leads, up to a coverage $\theta_H = 1.0$, to the formation of lattice gas structures,[4] which are followed by a (1×2) structure whose coverage was determined to be $\theta_H = 1.5$.[5] The LEED pattern of this phase is characterized by sharp and intense fractional-order spots as first reported by Taylor and Estrup[6] who already suggested that the latter are caused by a reconstruction of the substrate lattice. More recently, it was the subject of various investigations.[7-12] It should not be confused with another (1×2)H reconstruction in this system formed at $T > 200$ K which, however, exhibits a high degree of disorder as evident from the elongated half-order LEED beams and which is distinctly different in its thermodynamic and kinetic properties.[11] Earlier (unsuccessful) attempts at a LEED structure analysis were concerned with this "streak" phase, the real structure of which is still unknown.[13-15]

Details of the experimental setup and procedures can be found elsewhere.[4] The (1×2) phase was formed by exposure of the clean Ni(110) surface to 2L H_2 (1 L $= 10^{-6}$ Torr sec) at 120 K. The LEED intensity-voltage (I-V) data were recorded by the use of a computer-interfaced video system.[16] Normal incidence of the primary beam was verified by a comparison of the spectra from four symmetrically equivalent beams, which procedure proved to be very sensitive towards small angular deviations. The final experimental data were obtained by averaging of the I-V spectra from beams which are symmetrically equivalent at normal incidence. In total, eleven nonequivalent beams, six integral- and five fractional-order beams, were used for the structural analysis.

Calculations of the I-V data were performed by use of the layer-doubling scheme for the interlayer multiple scattering.[17] The topmost two layers, and in the case of the "buckled" structures in the "missing row" models (see below), in addition the third layer, were treated each as a combined layer. The nonstructural parameters, computational procedures, and R factors used for quantitative evaluation of the agreement between experimental and calculated I-V spectra are as described before.[18,19] In total, up to five structural parameters were systematically varied in the calculations, as indicated in Fig. 1. Scattering from the adsorbed H atoms was neglected, since the I-V spectra are dominated by scattering from the metal atoms if their reconstruction gives rise to corresponding superstructure beams.[18,19]

Figure 1 also displays the two basic structural models investigated, the missing-row (MR) and row-pairing (RP) models. In a first attempt the spacings D_{12}, D_{23}, and D_{34} between the layers marked by the indices and the lateral shift (LS) were systematically varied, without any obvious success: The optimum R factors (R_{ZJ}, Zanazzi-Jona R factor; R_P, Pendry R factor[18]) were poor ($R_{ZJ} \geq 0.32$, $R_P \geq 0.55$), and the calculated data

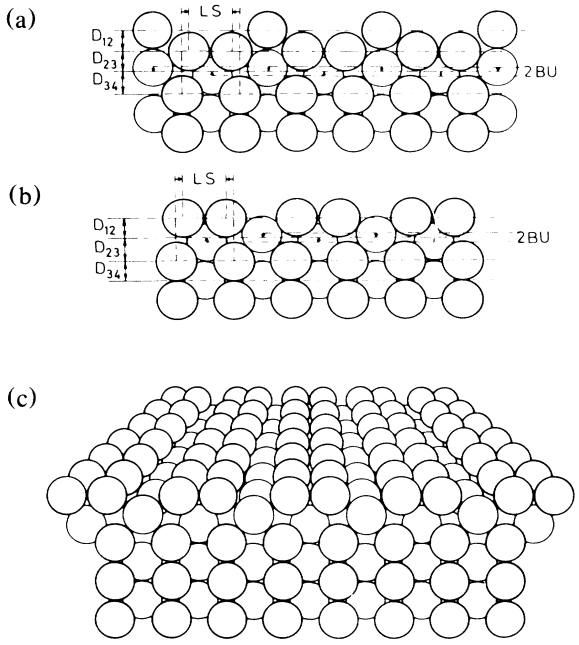

FIG. 1. Model of H-induced (1×2) reconstruction of Ni(110): (a) cut along the $(1\bar{1}0)$ plane for the missing-row (MR) (top) and the row-pairing (RP) (bottom) models together with their structural parameters; (b) perspective view of the buckled (RP) reconstructed surface.

provided no preference for either of the two models. In particular, a series of characteristic structures in the experimental I-V spectra were missing in *all* of the spectra calculated on this basis. This indicated that at least one additional structural parameter with considerable impact on the calculated data was still missing in the models checked so far. (Variations of the nonstructural parameters such as V_0, V_i, θ_D had no noticeable effect on the spectra.)

In a subsequent set of calculations, vertical displacements (buckling) in the second (third) layer for the RP model (MR model) were tentatively introduced. Figure 2 shows a series of I-V curves for two beams calculated for various buckling amplitudes; the effect is obvious. In particular, this additional parameter leads to the appearance of new maxima in the I-V curves, rather than to a general shift of the already existing ones as observed upon mere variation of the interlayer spacings. As a consequence of the improved agreement between experimental and calculated spectra the R factors decrease substantially and now permit a decision between the MR and RP models: For the RP model minimum R factors around $R_{ZJ}=0.15$ and $R_P=0.38$ are reached for the following structural parameters:

$D_{12}=1.27$ Å, $D_{23}=1.31$ Å, $D_{34}=1.25$ Å,

BU $=0.25$ Å, LS $=0.30$ Å.

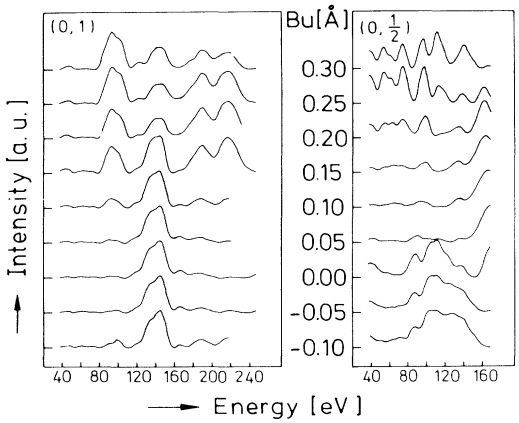

FIG. 2. Response of the I-V curves of the (01) and the $(0\frac{1}{2})$ beams upon variation of the buckling amplitude BU from -0.1 to $+0.3$ Å ($D_{12}=D_{23}=D_{34}=1.246$ Å, LS $=0.4$ Å)

For the MR model, on the other hand, the R factors basically remain at their former values. The error bars based on a statistical analysis of the data are about 0.02 Å, but may be larger because of systematic errors caused by the influence of the adsorbed hydrogen or distortions in deeper layers which have been neglected here (see below).

The variation of the R_P factors with different structural parameters is displayed in Fig. 3; in each set one parameter is varied while the other ones are kept fixed at or close to their optimum values. Optimization of the R factor is in reality, of course, not so straightforward since the effects of the various structural parameters on the R factor are interrelated, and as a consequence the minimum of R indeed has to be sought in a multidimensioned space. It is, however, for example quite evident from Fig. 3(e) that the R factors react very sensitively upon variations of the buckling parameters BU. Because of convergence problems BU could not be increased beyond 0.3 Å at these particular values of D_{23} and D_{34}, but even then the minimum in Fig. 3(e) (for the indicated values of the other parameters) is clearly visible.

Figure 4 shows the set of calculated I-V curves with the minimum R factors together with the experimental data. The associated structure [Fig. 1(b)] can be considered as being very reliable in view of the fact that for eleven nonequivalent beams essentially all observed features are reproduced by the calculations. Further improvement might possibly be achieved by introduction of additional lateral shifts of a row-pairing type within the third layer, but the resulting effect on the I-V curves would be small and presumably of a similar order of magnitude as the error introduced by neglecting scattering from the H atoms.

The present results have to be discussed in the light of previous attempts for a structure analysis of this phase:

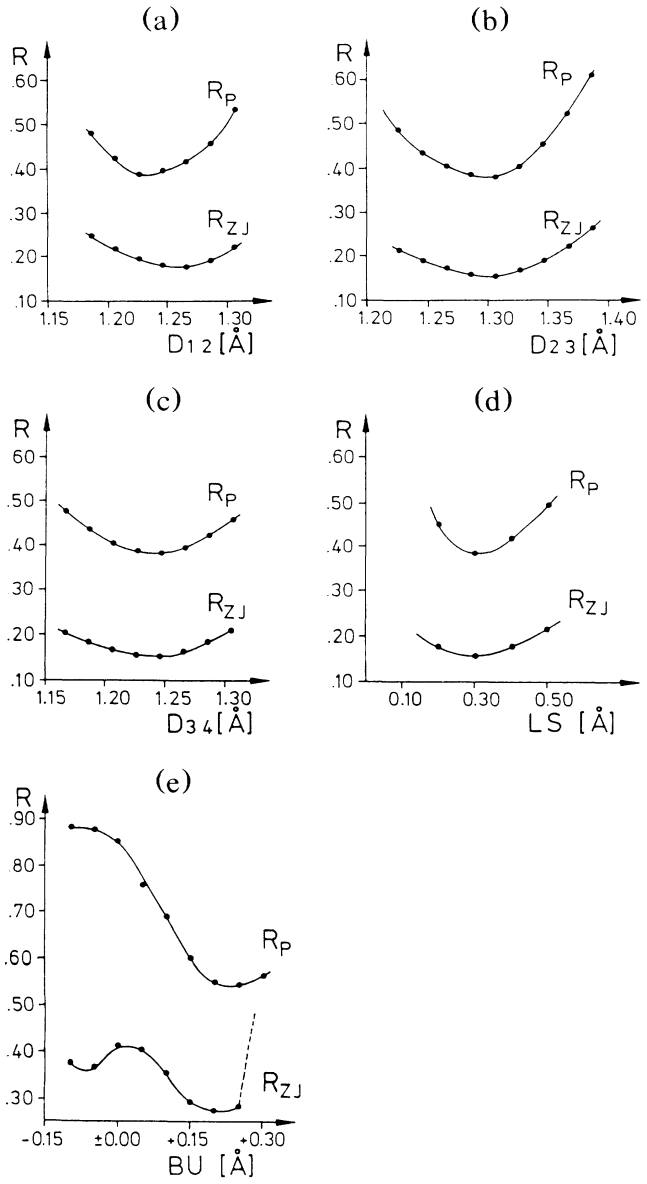

FIG. 3. R-factor dependence of the "best model" upon variation of one parameter: R_P and R_{ZJ} as functions of the interlayer spacings (a) D_{12}, (b) D_{23}, and (c) D_{34}, (d) the lateral shift LS and the (e) buckling parameter BU [(b), LS=0.4 Å; (e), parameters as in Fig. 2].

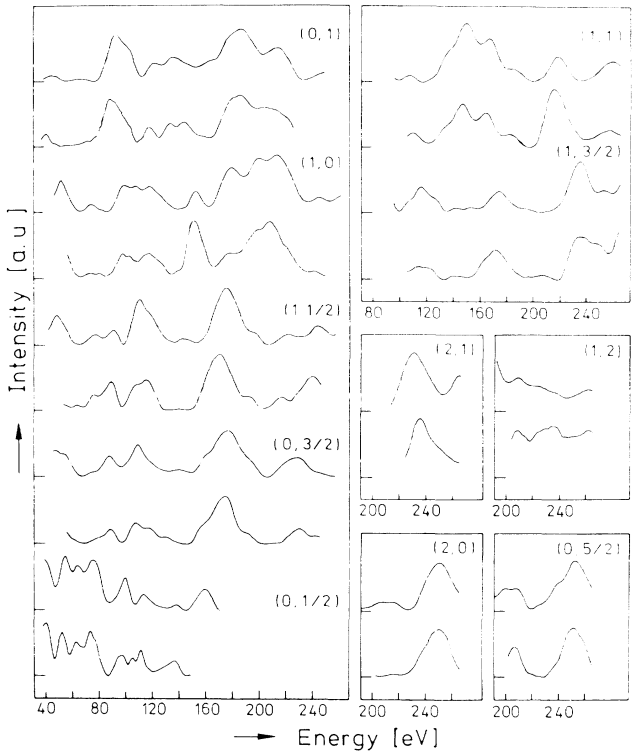

FIG. 4. Experimental (lower curves) and calculated (upper curves) I-V curves of the best row-pairing model (D_{12} =1.27 Å, D_{23}=1.31 Å, D_{34}=1.25 Å, LS=0.3 Å, BU =0.25 Å).

The early LEED work by Demuth[15] was based on data recorded at room temperature which are therefore due to the streak phase. More recently, Jones *et al.*[8] reported on a LEED analysis based on data taken at 150 K which, however, differ substantially from the experimental spectra of the present work—for reasons which are so far unknown. These authors favored a MR model (without buckling), for which, however, the R factors were unsatisfactorily high (R_P=0.63). He-beam scattering (which technique, however, senses no structural changes below the topmost layer) yielded a surface corrugation compatible with the structure presented here, and consequently the RP model was favored in this work.[7] From Rutherford backscattering (RBS) experiments a lateral displacement of all Ni atoms in the topmost layer by at least 0.1 Å was deduced, from which result the authors decided on the RP model.[9] Strong support for the validity of the RP model originates from recent low-energy ion-scattering experiments on the analogous (1×2)H/Pd(110) phase in which a MR model could clearly be ruled out.[20] An assignment of the position of the adsorbed H atoms is not directly possible on the basis of these data, but only adsorption sites as described in Ref. 11 allow physically reasonable H-H interatom distances.

The nearest-neighbor separation of Ni atoms in the (1×2)H reconstructed surface varies fom 2.40 to 2.66 Å, which covers only little more in range than what was found for the clean surface with its oscillatory interlayer relaxation (2.42–2.53 Å; bulk, 2.49 Å).[18] These small deviations from the clean-surface values, which would be further reduced by a slight third-layer row pairing, are largely a consequence of the buckling of the second layer

initiated by the lateral displacements of the atoms in the topmost layer. The latter effect is driven by the tendency of the surface to accommodate additional H atoms beyond $\theta_H = 1.0$ and to prevent strong H-H repulsions. The second (and probably also the third) layer responds to this change by optimizing again the Ni-Ni distances through buckling. Similar situations are found with the (1×2)-reconstructed, clean surfaces of Au(110) and Ir(110), which exhibit a missing-row structure,[2,3] as well as with a series of semiconductor surfaces[21] and are also established from recent theoretical treatments of the clean reconstructed metal surfaces.[22,23]

In conclusion, the excellent agreement between experimental and calculated LEED data for the (1×2)H-Ni(110) surface render the proposed structure model highly reliable. It involves a multilayer reconstruction leading to relief of internal strain, which would be the case if the gain in the adsorption energy were to affect only the configuration of substrate atoms in the topmost layer.

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