Surface relaxation of Rh{001}

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The relaxation of a clean Rh{001} surface is reexamined by means of analyses of three sets of low-energy electron diffraction (LEED) intensities collected in earlier experiments. The averaged results show that the first interlayer spacing is slightly contracted by (1.2±1.6%) with respect to the bulk spacing (1.902 Å) and that the second interlayer spacing is unrelaxed. These results are only a little different from those found by other authors in two previous LEED studies, and they lie in the range of the combined experimental errors of all the analyses. However, our results are in quite good agreement with a recent *ab initio* pseudopotential calculation of Morrison, Bylander, and Kleinman, who found ferromagnetism on the Rh{001} surface and a corresponding unusually small first-spacing relaxation.

We wish to report the results of a new determination of the relaxation of a clean {001} surface of Rh—a relaxation which has become an object of recent first-principles theoretical calculations and controversy. This controversy will be described below after a brief recount of the history of work on the relaxation of Rh{100}.

Watson and co-workers[1] were the first, in 1978–1979, to study the relaxation of a clean Rh{001} surface. They did so by means of quantitative low-energy electron diffraction (LEED) intensity analysis, and found a small expansion (1±0.9%) of the first interlayer spacing d_{12} with respect to the bulk spacing d_{bulk} (1.902 Å). Ten years later, in the course of a study of oxygen adsorption on Rh{001}, Oed *et al.* reexamined the relaxation of the clean surface.[2] They also used quantitative LEED and essentially confirmed the results of Watson and co-workers, finding a small expansion (0.5±1%) of d_{12} and practically no change in the second interlayer spacing d_{23} (0±1.5%).

These experimental results were later put into question by a theoretical study of Feibelman and Hamann (FH),[3] who used first-principles local-density-functional calculation methods. Their linearized augmented plane-wave total-energy calculation predicted that a clean Rh{001} surface should exhibit a 5.1% *contraction* of the first interlayer spacing. Arguing that their state-of-the-art electronic-structure calculations had been shown to predict bond lengths accurately to 1% or 2%, FH speculated that both the LEED data of Watson and co-workers and Oed *et al.* had unknowingly been collected on hydrogen-covered Rh surfaces. FH calculated, in fact, that an adsorbed monolayer of H would reduce the contraction of d_{12} to about 1.4%. However, FH did not do a spin-polarized calculation, hence did not allow the possibility of magnetic surface layers. Magnetic surface layers expand the volume per atom and the layer spacings: e.g., first-principles calculations on bulk Rh as a function of volume show that the ferromagnetic phase occurs and becomes the ground state at an atomic radius 14% larger than the nonmagnetic equilibrium radius.[4]

The most recent development is a theoretical study of Morrison, Bylander, and Kleinman (MBK),[5] who carried out *ab initio* spin-polarized pseudopotential calculations of nine-layer Rh{001} films. These authors found that the two top atomic layers on Rh{001} are ferromagnetic, and that the attendant magnetic pressure causes d_{12} to expand with respect to what it would be in the nonmagnetic case. Thus, the calculated multilayer relaxation involves a small contraction of d_{12} (−1.52%), a small expansion of d_{23} (+0.98%), and smaller contractions of the third and fourth layer spacings. The calculated relaxation of d_{12} is still outside the quoted error limits of the experimental studies, but the discrepancy between theory and experiment has been greatly reduced.

We collected LEED intensity data from clean Rh{001} about one year ago on three different occasions, not for the purpose of determining the surface relaxation, but for the purpose of characterizing the clean surface prior to experiments on the growth of epitaxial thin films of other metals. These data permit another determination of the relaxation of Rh{001}. We have no direct information on surface coverage by hydrogen, but we can give a plausible argument that such a coverage was not significant. In view of the present theoretical controversy, it seemed worthwhile to use our data in order to check the previous LEED results. Since our results show still closer correspondence to the MBK relaxations than previous LEED studies, and since the occurrence of magnetic surface layers on nonmagnetic bulk crystals is unusual, a Brief Report seems justified.

We calculated the LEED intensities from Rh{001} with Jepsen's CHANGE program.[6] We used the Rh potential of Moruzzi, Janak, and Williams;[7] 8 and 10 phase shifts (see below); 69 beams up to 500 eV; a constant inner potential $V_0=10+4i$ eV; and a root-mean-square amplitude of atomic vibrations $\langle u^2\rangle^{1/2}=0.15$ Å. We made a first series of calculations with d_{12} varying from 1.84 to 1.92 Å in steps of 0.02 Å (recall that $d_{\text{bulk}}=1.902$

Å), and we varied d_{23} from 1.86 to 2.02 Å also in steps of 0.02 Å. Our routine procedure consists in evaluating the agreement between theoretical and experimental $I(V)$ curves with three reliability factors, viz., R_{VHT} (Ref. 8), r_{ZJ} (Ref. 9), and R_P (Ref. 10), and confirm the fit by visual evaluation. With the first series of calculations all three R factors were minimized at d_{12} values *smaller* than d_{bulk} and d_{23} values equal to or somewhat larger than d_{bulk}. The r_{ZJ} factor, in particular, was minimized for $d_{12}=1.82$ Å and $d_{23}=1.96$ Å, but the fit to experiment was unacceptably poor by the visual evaluation, and as a consequence r_{ZJ} was no longer used in the subsequent analysis. (The occasional failure of one or the other of the three R factors is not an uncommon phenomenon that we have repeatedly reported earlier.[11])

In the second stage of the analysis we varied d_{12} from 1.832 to 1.912 Å in steps of 0.010 Å, and d_{23} from 1.862 to 1.942 Å also in steps of 0.01 Å. The analysis was done twice: once for calculations with 8 phase shifts and once for calculations with 10 phase shifts. The corresponding $I(V)$ spectra are visually indistinguishable from one another. The results for all three experimental sets tested are summarized in the top six rows of Table I. We note that the use of 10 versus 8 phase shifts affects only *some* of the parameter values by at most 0.006 Å (30 times less than the experimental error of 0.03 Å), and that the average values are identical in the two cases. The surprising outcome is that in both analyses five of the six d_{12} values determined here correspond to small *contractions* of the first interlayer spacing with respect to d_{bulk}. Not having any reason to prefer any one of the three experiments over another, or any of the two R factors over the other, we average the parameter values found in each case to give the final result (also listed in Table I in the seventh and eighth rows): $d_{12}=1.88\pm0.03$ Å, i.e., $(d_{12}-d_{\mathrm{bulk}})/d_{\mathrm{bulk}}=(-1.16\pm1.6)\%$ and $d_{23}=1.90\pm0.03$ Å, i.e., $(d_{23}-d_{\mathrm{bulk}})/d_{\mathrm{bulk}}=(0\pm1.6)\%$. The $I(V)$ curves calculated with these average values of the parameters are compared to the three sets of experimental data in Fig. 1. The results found by Watson and co-workers, Oed *et al.*, and by FH and MBK are also listed, for convenience, in the last four rows of Table I.

There is no contradiction between the older and the present experimental results—they all agree with one another within the combined error bars. What is interesting is that our results consistently show a slight

TABLE I. The top six rows (after the heading) show the values of the first (d_{12}) and second (d_{23}) interlayer spacing on Rh{001} as found in this work by minimization of the R_{VHT} and the R_P reliability factors in three experiments labeled 1, 2, and 3. Two values are given for each quantity: the first was found with calculations with 10 phase shifts, the second (in parentheses) was obtained with calculations with 8 phase shifts. The seventh row shows the averages in Å while the eighth row lists the corresponding changes from the bulk value (1.902 Å) in percent, i.e., $[(d_{ik}-d_{\mathrm{bulk}})/d_{\mathrm{bulk}}]\times100$. The corresponding results of earlier LEED analyses by Watson and co-workers and Oed *et al.* are listed in rows 9–12. The last four rows show the results of calculations by Feibelman and Hamann (FH) and by Morrison, Bylander, and Kleinman (MBK).

Experiment	R factor	d_{12} (Å)	d_{23} (Å)
1	$R_{\mathrm{VHT}}=0.32(0.32)$	1.880(1.880)	1.904(1.908)
	$R_P=0.32(0.36)$	1.888(1.894)	1.888(1.888)
2	$R_{\mathrm{VHT}}=0.28(0.28)$	1.860(1.854)	1.914(1.916)
	$R_P=0.28(0.32)$	1.878(1.878)	1.896(1.896)
3	$R_{\mathrm{VHT}}=0.37(0.37)$	1.884(1.882)	1.910(1.910)
	$R_P=0.35(0.38)$	1.912(1.906)	1.890(1.894)
	Averages	1.88±0.03	1.90±0.03
		(−1.16±1.6%)	(0±1.6%)
Watson and co-workers[a]		1.92±0.02	
		(+1±0.9%)	
Oed *et al.*[b]		1.91±0.02	1.90±0.03
		(+0.5±1%)	(0±1.5%)
Theory	FH[c]	1.805	1.892
		(−5.1%)	(−0.5%)
Theory	MBK[d]	1.873	1.921
		(−1.52%)	(+0.98%)

[a]Reference 1.
[b]Reference 2.
[c]Reference 3.
[d]Reference 4.

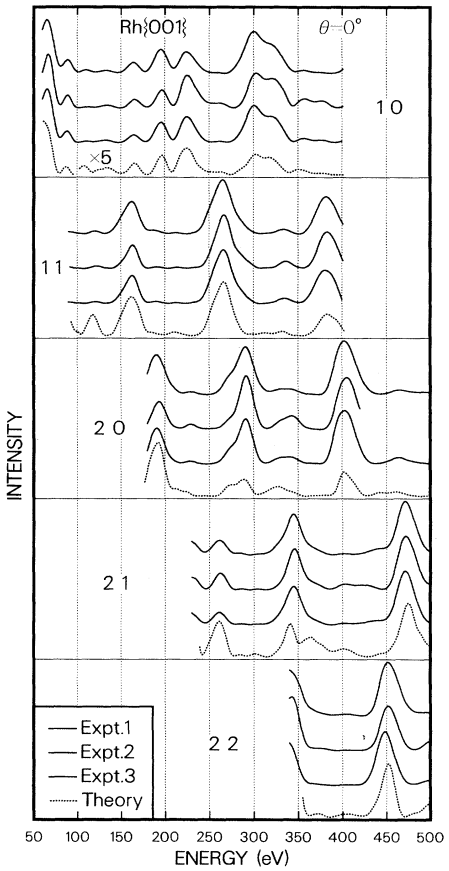

FIG. 1. Theoretical (dashed) and experimental (solid) $I(V)$ spectra of clean Rh{001}.

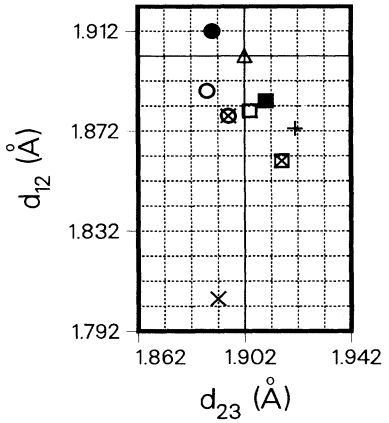

FIG. 2. Relaxation of Rh{001}. The squares and the circles are experimental results (from the analysis with 10 phase shifts): the squares from minima of the R_{VHT} factor, the circles from minima of the R_P factor; empty symbols are from experiment 1, symbols with the × are from experiment 2, solid symbols from experiment 3. The + and the × indicate the theoretical predictions of MBK and FH, respectively; the triangle marks the bulk value. Note that the spacing between dashed lines is 0.01 Å.

compression of d_{12}, as opposed to the slight expansion found in the two earlier LEED studies. We compared our experimental $I(V)$ curves with those published by both Watson and co-workers and Oed *et al.*: we found fair agreement with the former and excellent agreement with the latter. We note that analysis by Oed *et al.* involved 8 $I(V)$ curves *versus* our 4, and an energy range extending from 50 to 600 eV *versus* our range from 50 to 500 eV, all of which should increase the confidence level of results by Oed *et al.*, but the analysis by Oed *et al.* made use of only one R factor (R_P). It is difficult to establish with certainty the causes of the differences in the structure results, but it is probable that they lie in the different experimental data. In any case the differences are small—smaller in fact than the differences found in an earlier project involving comparisons between experimental LEED $I(V)$ curves from Cu{001} taken in five laboratories.[12]

The interesting new fact is that our experimental results are in quite good agreement with the predictions of MBK, closer than previous LEED results. A graphic representation of the scatter of the six different structure determinations done in this work is given in Fig. 2, which shows that all but one of the experimental d_{12} values are somewhat larger, and all the experimental d_{23} values are somewhat smaller, than the MBK value (the cross in Fig. 2), but that all experimental results lie within approximately 0.04 Å of MBK's theoretical prediction.

There remains the question of hydrogen coverage, which may possibly have played a role in our experiments. While we cannot exclude this possibility, we consider it rather improbable for the following reason. Richter *et al.*[13] found that a 2-L exposure (1 L$=10^{-6}$ Torr s) of Rh{001} to hydrogen gas is adequate to saturate the surface with hydrogen. Our data were collected in all three experiments at a pressure of 1×10^{-10} Torr between 1 and 3 h after the sputtering and annealing processes needed to prepare a clean Rh{001} surface. Assuming that the residual pressure in our experimental chamber was due exclusively to H_2 and that the sticking coefficient was unity, we find that it would have taken more than 5.5 h to saturate the Rh{001} surface. Hence, at most only about one half of our surface would have been covered with hydrogen—and the same coverage would have had to be coincidentally present in the experiment of Oed *et al.*, given the excellent agreement between the corresponding sets of experimental data.

We conclude therefore that the results of the LEED studies done in three different laboratories are basically in agreement with one another and very probably give the true relaxation of clean Rh{001} within the assigned error bounds. Hence, these results support the theoretical conclusion that the magnetic pressure generated on the clean surface reduces the relaxation of the first interlayer spacing from a compression of 5.1% (as calculated by FH) to a compression of 1% to 1.5% (as calculated by MBK).

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