

Interpretation of O binding-site preferences on close-packed group-VIII metal surfaces

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Screening of O atoms adsorbed on transition metals is accomplished in part by d -electron redistribution in near-surface, inter-metal-layer bonds. First-principles calculations imply that this is the source of O's preferences for fcc adsorption sites on Pt(111) and hcp hollows on Ru(0001). In both instances, O prefers the site for which screening weakens interlayer bonds the least. Which site this is depends on whether the d states repopulated by screening are nonbonding or antibonding. [S0163-1829(98)07048-9]

I. INTRODUCTION

Tools that provide insight into the forces underlying surface structure are needed to derive full value from our increasing ability to measure and, computationally, to predict adsorption geometries. I argue here by example that the general correlation between bond strength and bond length is such a tool. Completing a discussion begun in an earlier paper,¹ I show that calculated bond lengths point to a consistent, novel interpretation of O-atom site preferences on both Pt(111) (Ref. 2) and Ru(0001).³

At low coverages, on close-packed group-VIII transition-metal surfaces, chalcogen atoms generally adsorb in the threefold hollows that continue the lattice (see Table I).⁴ This regularity, one is inclined to guess, is favored by a preponderance of unsaturated valence, or of surface "frontier orbitals"^{5,6} in lattice-continuation sites, i.e., in fcc hollows on fcc(111) surfaces and in hcp sites on hcp(0001) planes. But this heuristic assumption is contradicted by first-principles, density-functional theory⁷ (DFT) based structure calculations. Specifically (see Table II), although O's preference for the lattice-continuation site is several tenths of an eV, for both metals,⁸ *calculated O-Pt bond lengths for fcc and hcp binding sites on Pt(111) differ by only $\sim 0.5\%$, and the same is true on Ru(0001).*

This surprising outcome points to a source of O's site preferences other than bonding to frontier orbitals. If, for example, the 0.44 eV preference on Pt(111) were the result of Pt bonds dangling preferentially into fcc hollows, then one would certainly expect the O-Pt bond length at these sites to be substantially shorter than in the hcp bonding geometry. But it is not.

Structurally, the leading difference between fcc and hcp sites is the registry of first and second metal-atom layers below the adatom. This suggests distinguishing sites according to how effectively the complex formed by an adatom and its three nearest neighbors binds to the remainder of the metal substrate,⁹ and learning the answer by examining computed or measured metal-metal bond lengths. In what follows, I therefore compare the bonds between an ad-O's first and second metal-layer neighbors. I examine charge-density contour plots and corresponding bond lengths, and interpret

the results in light of the bonding character of the d states near the Fermi level.

The plots reveal that screening either adds to or diminishes d -electron charge between an ad-O's first- and second-layer metal neighbors, depending on their relative positions. The corresponding effect on bond length and strength is substantial if the d states that are filled or emptied are antibonding in nature. When they are nonbonding, however, it is virtually nil, and this difference is enough to explain why O prefers different sites on Ru(0001) and Pt(111).

The remainder of this note is organized as follows. Section II is devoted to details of the electronic-structure calculations that underlie the argument. In Sec. III, I show that the computed adsorption geometries are in satisfactory agreement with experiment. I discuss the systematics of the calculated bond lengths versus adsorption site in Sec. IV. Finally in Sec. V, I explain how d -band filling allows one to extend the screening-based interpretation¹ of O's fcc preference on Pt(111) to its hcp preference on Ru(0001).

II. DETAILS OF THE CALCULATIONS

The results presented below were obtained using the efficient and accurate *ab initio* total-energy and molecular-dynamics package, VASP (Vienna *Ab initio* simulation package).¹⁰⁻¹² VASP is particularly well-suited for systems involving "strong pseudopotential atoms," such as O, Pt, and Ru, because its optimized, ultrasoft pseudopotential database assures absolute convergence of total energies to ~ 10 meV, with a plane-wave basis-set cutoff of only 29 Ry.

In the spin-averaged, scalar-relativistic calculations re-

TABLE I. Summary of observed chalcogen site preferences on group-VIII metals' close-packed surfaces after Ref. 4.

Adatom	Metal	Surface type	Preferred site
O	Ni, Rh, Ir, Pt	fcc(111)	fcc
S	Pd	fcc(111)	fcc
Se	Ni	fcc(111)	fcc
O	Ru	hcp(0001)	hcp

TABLE II. Computed per-atom binding energy differences and O-metal bond lengths for $p(2 \times 2)$ -O overlayers on Pt(111) and Ru(0001).

System	ΔBE (fcc-hcp)	R_{O-M} (fcc)	R_{O-M} (hcp)
O/Pt (LDA)	0.44 eV	2.02 Å	2.03 Å
O/Ru (LDA)	-0.61 eV	2.00 Å	1.99 Å
O/Ru (GGA)	-0.57 eV	2.03 Å	2.02 Å

ported here, I model semi-infinite crystals as seven-layer slabs, fixing the lower three slab layers in their bulk atomic arrangement, and allowing the upper four to relax in the presence of O. Exchange and correlation (XC) effects are represented either in the local-density approximation⁷ (LDA), by the Ceperley-Alder XC potential,¹⁵ or, for comparison with the LDA in the case of O/Ru, using the Perdew-Wang '91 generalized gradient approximation (GGA).¹⁴

I fix the lattice parameter for each slab via DFT optimization of the corresponding bulk metal.¹⁵ I sample the irreducible part of the surface Brillouin zones of $p(2 \times 2)$ -O/Pt(111) and $p(2 \times 2)$ -O/Ru(0001) slabs with seven equally spaced k vectors. To accelerate electronic relaxation, I adopt the Fermi-level smearing approach of Methfessel and Paxton,¹⁶ using a Gaussian width of 0.2 eV. In all cases I optimize geometries until forces on unconstrained atoms are smaller than 0.03 eV/Å.

III. CALCULATED VERSUS EXPERIMENTAL ADSORPTION GEOMETRIES

Before attempting to use interatom distances as an interpretive tool, it is important to check that DFT calculations give a reasonable account of O adsorption geometries measured on Pt(111) and Ru(0001). On Pt(111), O saturates in a $\frac{1}{4}$ ML, $p(2 \times 2)$ overlayer.² On Ru(0001), both $\frac{1}{4}$ ML $p(2 \times 2)$ and $\frac{1}{2}$ ML $p(2 \times 1)$ structures can be prepared by O₂ deposition,^{3,17} of which only the former is discussed here. The most basic consistency check is to see that DFT predicts correct binding sites. Table II shows that it does, but also that the site-preference energies are large compared to what one might expect for an effect controlled by the O adatoms' second neighbors.¹⁸

Given that DFT predicts site preferences correctly, I now compare computed bond lengths (see Tables III–V) to corresponding results from LEED analysis.^{2,3} In order to make the comparison sensibly, given that neither the LDA nor the GGA generally predicts absolute lattice parameters to better

TABLE III. Comparison of experimental and calculated O-metal bond lengths, R_{O-M} , for $p(2 \times 2)$ -O overlayers on Pt(111) and Ru(0001), in each case normalized to the nearest-neighbor distance in the bulk metal $R_{nn}(\text{Ru, GGA}) = 2.663$ Å.

System	Site	$R_{O-M}^{\text{expt.}}/R_{nn}^{\text{expt.}}$	$R_{O-M}^{\text{calc.}}/R_{nn}^{\text{calc.}}$
O/Pt (LDA)	fcc	0.728 ± 0.02^a	0.735
O/Ru (LDA)	hcp	0.766 ± 0.02^b	0.766
O/Ru (GGA)	hcp	0.766 ± 0.02^b	0.759

^aReference 2.

^bReference 3.

TABLE IV. Effect of a $p(2 \times 2)$ -O adlayer on interlayer Pt-Pt distances. R_{bc} and R_{bd} are distances between Pt atoms as indicated in the schematic of Fig. 1. R_{12}^{cln} is the distance between nearest Pt atoms in layers 1 and 2 of *clean* Pt(111). For each O adatom there are three b - c bonds and six b - d bonds.

O site	Method	$R_{bc}/R_{12}^{\text{cln}}$	$R_{bd}/R_{12}^{\text{cln}}$
hcp	LDA	1.027	1.008
fcc	LDA	0.973	1.024
fcc	LEED ^a	0.974 ± 0.02	1.011 ± 0.02

^aReference 2.

than $\sim 1\%$, I normalize the O-metal distances in Table III to the nearest-neighbor spacing in the corresponding bulk metal. In Tables IV and V, for the sake of the argument presented below, I compare dimensionless ratios of distances, for which such normalization is unnecessary.

Tables III–V confirm, within experimental error bars,¹⁹ that the DFT calculations account *quantitatively* for the geometries of the $p(2 \times 2)$ -O/Pt(111) and $p(2 \times 2)$ -O/Ru(0001) adsorption systems.²⁰ Thus, the details of the density-functional results *must* embody an explanation of why O atoms' site preference differs for the two different metals. The only question is, which details?

IV. hcp VERSUS fcc ADSORPTION GEOMETRIES

As noted in Sec. I, the remarkable feature of the geometries computed for $p(2 \times 2)$ -O/Pt(111) and $p(2 \times 2)$ -O/Ru(0001) is that despite substantial site-preference energies, the O-metal bond length is site-independent to $\sim 0.5\%$ in both cases (cf. Table II). The “message” of this result is clear: since stronger bonds are generally shorter, and weaker ones generally longer, *O-metal bonds are not the main source of the large site-preference energies on either surface.*

What is, then? As initially proposed in Ref. 1, a reasonable idea is that the bonds between each O adatom's first- and second-neighbor metal atoms determine the preferences. The logic is simple: to leading order it is precisely the different orientations of these bonds that differentiate fcc from hcp binding sites.

Referring to the labeling scheme of the schematics in Figs. 1 and 2, consider the results presented in Tables IV and V.²⁰ In both the hcp and fcc binding configurations, an O

TABLE V. Effect of a $p(2 \times 2)$ -O adlayer on interlayer Ru-Ru distances. R_{bc} and R_{bd} are distances between Ru atoms as indicated in the schematic of Fig. 2. R_{12}^{cln} is the distance between nearest Ru atoms in layers 1 and 2 of *clean* Ru(0001). For each O adatom there are three b - c bonds and six b - d bonds.

O site	Method	$R_{bc}/R_{12}^{\text{cln}}$	$R_{bd}/R_{12}^{\text{cln}}$
hcp	LEED ^a	1.05 ± 0.03	0.99 ± 0.03
hcp	LDA	1.051	1.000
hcp	GGA	1.050	0.998
fcc	LDA	1.006	1.031
fcc	GGA	1.004	1.030

^aReference 3.

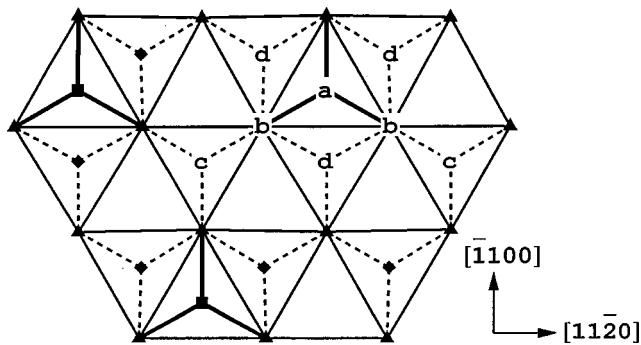


FIG. 1. Schematic top view of the fcc bonding geometry. Squares and the label a represent O nuclei. Triangles and the label b represent outer-layer metal nuclei. Diamonds and the labels c and d represent subsurface layer metal nuclei. Axis labels are for O adsorbed on an hcp(0001) surface. For an fcc(111) surface, the diagram would look the same but the x - and y -axis labels would be replaced by $[10\bar{1}]$ and $[\bar{1}2\bar{1}]$. Primitive vectors for the 2×2 unit cell run from one square to the other, and from a square to a .

adatom has three nearest neighbors (labeled b) in the outermost metal layer, and each of these metal atoms forms three bonds to atoms (labeled c and d) in the second layer. (Note that because it is directly below atom a , subsurface atom c is invisible in Fig. 2.) In both sites, the nine bonds between the b atoms and the next neighbors in the layer below come in two “flavors.” There are three b - c bonds, each of which lies in a plane normal to the surface that passes through the O adatom. The remaining six, the b - d bonds, do not lie in such a plane.

Table IV shows that with O in fcc hollows on Pt(111), the b - c bonds shrink by 2.7% relative to the clean surface, while the b - d bonds expand by 2.4%. If the O is in hcp sites instead, then both the b - c and the b - d bonds expand. The implication is that in the fcc geometry, weakening of the b - d bonds is compensated for by strengthening of the b - c interaction. This makes fcc adsorption favorable on Pt(111) compared to the hcp configuration, in which O adsorption weakens both the b - c and the b - d bonds.

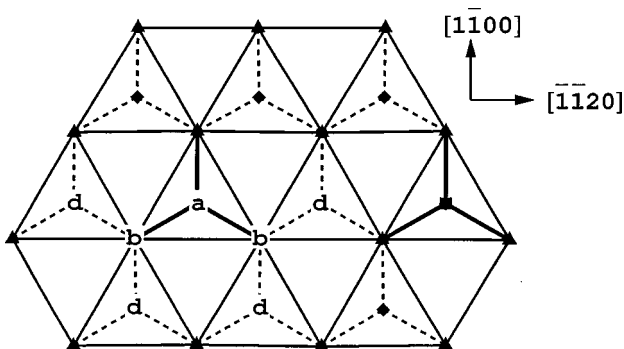


FIG. 2. Schematic top view of the hcp bonding geometry. Squares and the label a represent O nuclei. Triangles and the label b represent outer-layer metal nuclei. Diamonds and the label d represent subsurface layer metal nuclei. The subsurface atom, c , directly beneath the O, is not visible in this view. Axis labels are for O adsorbed on an hcp(0001) surface. For an fcc(111) surface, the diagram would look the same but the x - and y -axis labels would be replaced by $[\bar{1}01]$ and $[1\bar{2}1]$.

Table V shows why the site preference is different on Ru(0001). On this surface, if the O atoms are in fcc hollows, though the b - d bonds are expanded by an amount (3.1% in LDA) comparable to their expansion for O on Pt(111) (2.4%), the b - c bond lengths now hardly change at all. Thus whereas the fcc adsorption geometry is favorable for O/Pt(111) because b - c bond strengthening compensates for b - d bond weakening, in the case of Ru(0001) there is no compensation. The six b - d bonds associated with each ad-O weaken, and that is all.

If O resides in an hcp site on Ru(0001), a similar effect occurs. Now, however, only the three b - c bonds expand as a result of adsorption, while the lengths of the six b - d bonds remain virtually the same.²⁰ Thus, although it remains to learn why the pattern of bond-length changes on Ru differs from that on Pt(111), the results imply that the hcp site is favored on Ru(0001) because O adsorption in that site only weakens three interlayer Ru-Ru bonds, while six bonds are weakened if the adsorption site is fcc.

V. BOND CHARACTER AND O-INDUCED BOND STRENGTH CHANGES

In Ref. 1, I attributed the changes that O induces in interlayer Pt-Pt bonds to the combined effects of screening and of the purely antibonding character of Pt's near-Fermi-level d bands. Screening, an electrostatic effect, is unlikely to differ much at a Ru as against a Pt surface. Thus it makes sense to see if O's hcp site preference on Ru(0001) might result from Ru's lying near the middle of the $4d$ transition series, such that both antibonding and nonbonding bands lie near its Fermi level.²¹

The argument for the fcc site preference on Pt(111) starts from the idea that because an adsorbed O is somewhat negatively charged, the d hole on each of its nearest neighbors will orient along its bond to the O.¹ As anticipated, Fig. 3 shows that this effect is also operative for O adsorption on Ru. The interesting question, then, is how pushing d electrons away from the O- b bonds affects the strength of the b - c and b - d bonds.

In the Pt case the consequence of the population changes is clear, because the bands involved in screening, those that lie near the Fermi level, are antibonding. Bonds that lose d electrons must increase in strength and shorten, while those that gain d charge weaken and lengthen. This statement accounts entirely for the results summarized in Table IV. Specifically, in fcc-hollow adsorption on Pt(111), the b - c bonds lose d charge [see Fig. 3(a), Ref. 1] and shorten. At the same time, the b - d bonds in the fcc case and the b - c and b - d bonds for hcp O adsorption on Pt(111) acquire charge and lengthen.

The “volcano curve” of cohesive energy versus $4d$ -band filling,²² reproduced in Fig. 4, offers the key perspective on what makes Ru different from Pt. Cohesion peaks in the middle of the $4d$ series where all bonding states are full and nonbonding bands are partially occupied. Beyond the peak, and approaching the noble-metal side of the $3d$, $4d$, or $5d$ transition series, cohesion diminishes once nonbonding states are filled and antibonding states begin to be occupied. Because Pt, like Pd, lies in column 10 of the Periodic Table, the bands at its Fermi level are purely antibonding. Ru (cf. Fig.

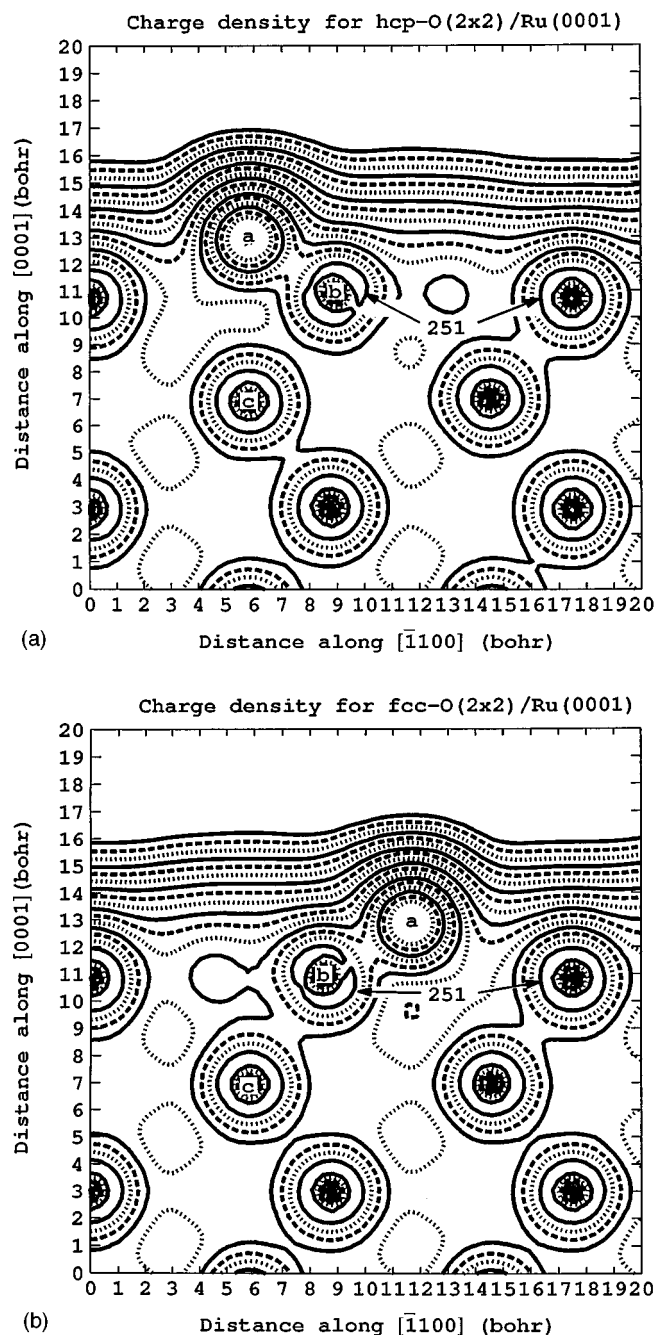


FIG. 3. Contours of constant charge density, for $O(2 \times 2)/Ru(0001)$, in a $(11\bar{2}0)$ plane. Panel (A): O adatoms, like that labeled *a*, lie directly above a subsurface layer Ru, labeled *c*. Thus, *a* is in an hcp hollow site. Panel (B): The O adatom, labeled *a*, is now in the fcc hollow. In both panels, the atom labeled *b*, in the outermost Ru layer, is one of *a*'s three nearest neighbors, and the charge density changes by the factor $10^{0.2}$, between successive contours. The contours labeled "251" correspond to 251×10^{-3} electrons/bohr³. They enclose a white region about each Ru nucleus, where the valence charge density, mainly *d*-electron charge, is maximal. Notice that, in panel (A), the "251" contour about atom *b* bulges along the bond between atoms *b* and *c*. In panel (B), the *d* charge on atom *b*, again repelled by the O nucleus, now bulges in a plane transverse to the *b-c* bond. Both panels correspond to LDA calculations using QUEST (see Ref. 18).

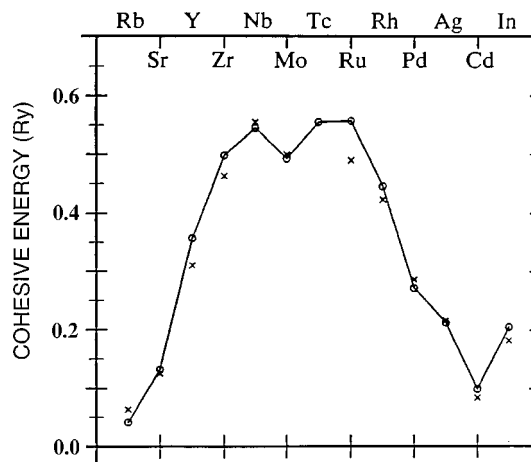


FIG. 4. LDA (circles) vs experimental (crosses) cohesive energies for the 4*d* metals (after Ref. 22).

4) sits just to the right of the peak in the 4*d* volcano curve. Accordingly, the bands near Ru's Fermi surface are of non-bonding as well as antibonding character.

That nonbonding states lie near the Ru Fermi level makes it easy to explain how the *b-c* bond lengths in fcc-site O adsorption and the *b-d* bond lengths in hcp site adsorption can be unchanged relative to the clean Ru(0001) surface. The reason is that nonbonding *d* electrons are what are removed from or added to these bonds, as the O adatoms are screened. On the other hand, the *b-d* bonds in fcc adsorption and the *b-c* bonds in the hcp case lengthen because they acquire antibonding rather than nonbonding charge.

VI. THE FUTURE

The ideas presented here may be useful in extending our understanding of adsorbate site preferences beyond the case of O on group-VIII metals. Recent theoretical progress, as well as intense interest in controlled epitaxial growth, point to *metal-on-metal* adsorption as a timely example. The present explanation of O site preferences on Ru(0001) and Pt(111) provides a physical sense of how band filling affects the adsorption of electronegative species. Recent calculations by Papadia *et al.*,²¹ based on tight-binding theory, suggest that band filling is also the key to understanding the site preferences of metal adatoms and ad-islands on transition-metal substrates. Fleshing out the results of Ref. 21 with first-principles calculations of charge redistributions, orbital occupations, and adsorbate-induced surface buckling would be of considerable interest.

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- ¹⁴J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991); J. P. Perdew and Y. Wang (unpublished). The VASP implementation of the GGA is fully self-consistent, including the incorporation of gradient corrections to the exchange-correlation potential in the pseudopotentials.
- ¹⁵For LDA Ru, $a=2.675$ Å and $c/a=1.581$, for GGA Ru, $a=2.722$ Å and $c/a=1.579$, and for LDA Pt, $a=3.911$ Å. Experimental room-temperature lattice constants for comparison are $a=2.71$ Å and $c/a=1.579$ for Ru and $a=3.92$ Å for Pt.
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- ¹⁹It should be borne in mind that error bars in LEED analyses do not provide any information concerning the potential systematic error level in applying an approximate scattering theory to extract geometry from electron scattering data. Nor is the error in the usual R -factor analysis statistical noise. Therefore there is no clear way to add errors quoted for different structural parameters. I obtained the error values in Tables III–V by computing maximum and minimum possible interatom distances, given the error bars quoted in Refs. 2 and 3.
- ²⁰Ru-Ru bond length changes, quoted in Sec. VI A of Ref. 1, for O/Ru were calculated relative to *ideal*, i.e., to unrelaxed, clean Ru(0001). Thus, it is not true that “Of the three bonds between each Ru atom adjacent to an O, and its neighbors in the second layer, LEED (i.e., Ref. 3) says that one is stretched 2.9% relative to the clean surface, but the other two are 2.4% contracted.” With Ru(0001)'s outer-layer relaxation taken into account, one is stretched about 5% and the others are virtually unchanged, as reported in Table V.
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