

### Comment on "Evidence for Two States of Chemisorbed Oxygen on Ni(100)"

In an attempt to characterize O on Ni(100), Upton and Goddard<sup>1</sup> (UG) identified two low-lying electronic states of a Ni<sub>20</sub>O cluster: the "oxide" and the "radical" states. A calculation on Ni<sub>20</sub>O<sup>+</sup>, intended to simulate higher coverage, gave an "oxide" state with a short  $R_{\perp} = 0.26 \text{ \AA}$ . Comparing calculated vibrational frequencies,  $\omega_e$ , to experiment,<sup>2</sup> UG concluded that the radical state represented  $p(2 \times 2)\text{O}$  and the oxide state  $c(2 \times 2)\text{O}$ . Our contention, based on theory and experiment, is that the  $p(2 \times 2)$  and  $c(2 \times 2)$  O structures are both "oxide" with normal  $R_{\perp}$ 's.

To test the adequacy of the Ni<sub>5</sub>O cluster we used and the limitations of UG's generalized valence-bond (GVB) treatment, we performed self-consistent-field (SCF) calculations using the same pseudopotential as UG and including only  $s$  functions on Ni. Our SCF results for  $R_{\perp}$ ,  $\omega_e$ , and  $\Delta E$ , the separation between radical and oxide states at their minima, are in excellent agreement with UG (Table I). The agreement also shows that the limited correlation included by UG does not significantly affect these properties. When we included Ni  $4p$  functions, however, the results did change, as shown. Our preliminary all-electron calculations on Ni<sub>5</sub>O show that these results are not an artifact of the pseudopotential.

Population analysis shows that O is more negative in the oxide ( $-1.32e$ ) than in the radical ( $-0.67e$ ) state in agreement with UG and a sure sign of difficulty since our SCF electron affinity (E.A.) for O,  $-0.58 \text{ eV}$ , is far from the experimental value,  $+1.46 \text{ eV}$ . We therefore treated correlation through an all single and double excitation configuration interaction (SDCI) for the Ni<sub>5</sub>O calculation. As a result of the more correct treatment of the oxygen anion, the SDCI results show a greatly stabilized oxide state (Table I). The E.A. for O is now  $+0.74 \text{ eV}$ , much closer to experiment. Improvements in the correlation treatment will further stabilize the oxide state. Thus, when these important factors, ignored by UG, are included, the oxide state is clearly much more stable and has a normal  $R_{\perp}$  of  $0.74 \text{ \AA}$ .

Four independent experimental studies of O on Ni(100) arrive at  $R_{\perp} \approx 0.9 \text{ \AA}$  for both  $p(2 \times 2)$  and  $c(2 \times 2)$  structures: surface extended-x-ray-absorption fine structure (SEXAFS),<sup>3</sup> low-energy electron diffraction, normal photoelectron diffraction (see Ref. 3 and Refs. 5, 8, and 16 therein), and He scattering.<sup>4</sup> A suggestion of a short  $R_{\perp}$  from an angular x-ray photoelectron spectroscopy

TABLE I. Summary of results.

	Radical state		Oxide state		$\Delta E$ (eV)
	$R_{\perp}$ ( $\text{\AA}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$R_{\perp}$ ( $\text{\AA}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	
Ni <sub>20</sub> O <sup>a</sup>	0.88	371	0.55	218	0.34
Ni <sub>20</sub> O <sup>+</sup> <sup>a</sup>	0.83	355	0.26	266	1.03
SCF Ni <sub>5</sub> O					
no $4p$	0.87	374	0.57	251	0.42
with $4p$	0.98	358	0.68	290	0.10
SDCI Ni <sub>5</sub> O	0.91	317	0.74	320	0.89
$p(2 \times 2)\text{O}$			0.9 <sup>b</sup>	430 <sup>c</sup>	
$c(2 \times 2)\text{O}$			0.9 <sup>b</sup>	310 <sup>c</sup>	

<sup>a</sup>Ref. 1;  $4p$  functions were not used.

<sup>b</sup>Ref. 3 (and references therein) and Ref. 4.

<sup>c</sup>Ref. 2.

copy (XPS) measurement<sup>5</sup> does not refer to O in the  $c(2 \times 2)$  structure, but to minority bulk oxide to which it is particularly sensitive.<sup>5</sup> The SEXAFS edge fine-structure,<sup>3</sup> ultraviolet photoelectron spectroscopy,<sup>6</sup> and XPS O(1s) binding energies<sup>6</sup> all indicate identical electronic character for  $p(2 \times 2)$  and  $c(2 \times 2)$  O.

In conclusion, we find no evidence for either a stable chemisorbed O radical state or an oxide state with an unusually short  $R_{\perp}$ . The difference in  $\omega_e$  between  $p(2 \times 2)$  and  $c(2 \times 2)$  structures, which both have  $R_{\perp}$  of  $\sim 0.9 \text{ \AA}$ , may simply be due to increased coverage effects.

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