# Summary Abstract: Surface vibrational resonances and the order–disorder transformation of the W(100) surface

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Reconstruction of the clean W(100) surface was originally observed with LEED when the crystal was cooled below room temperature.[1] The reconstructed surface exhibits sharp $c(2\times2)$ LEED spots which become weak and diffuse as the sample approaches room temperature.[2] LEED beam broadening and intensity reduction indicate a loss of long range order. MeV ion scattering experiments[3] suggest a structural model with W surface atoms displaced in a random manner corresponding to small domains. This is the first proposed disordered W(100) surface model since surface disorder was dismissed as unreasonable in Ref. 1. Adsorption of hydrogen at room temperature can restore long range order to the surface.[4] Low coverage hydrogen adsorption (0.3 monolayer) on W(100) also yields a $c(2\times2)$ LEED pattern, and saturated hydrogen produces a $p(1\times1)$ LEED pattern. The saturated surface is commensurate with the bulk, and several models for the low temperature and hydrogen induced $c(2\times2)$ surfaces have been proposed.[5,6]

We have investigated the W(100) surface with electron energy loss spectroscopy (EELS). EELS provides a wealth of information useful in characterizing this surface. Surface contaminants (C, O, CO) are detactable to $\sim1\%$ monolayer. The dipole modes of low coverage and saturated hydrogen occur at 155 and 130 meV, respectively.[6] In Fig. 1 several EEL spectra are shown on a logarithmic intensity scale. With an elastic peak resolution of 7 meV, a new vibrational mode is observed at 26 meV on the hydrogen saturated room temperature surface. The vibrational energy does not shift with deuterium adsorption indicating this mode is an intrinsic vibration associated with the W surface. Similar losses have been observed[7] on Cu(100) and Ni(110). In these cases, it has been proposed that extreme in the longitudinal bulk phonon dispersion within the Brillouin zone (a Van Hove singularity) leads to a gap in the probed density of states, and to the observed surface resonance in the EEL spectra. The longitudinal bulk phonon dispersion curve for W(100)[8] has a corresponding maximum at 26 meV. The intensity of the loss feature decreases in off-specular geometry, characteristic of dipole scattering. A calculation[9] of the phonon density of states for W(100) shows a local maximum near 26 meV for surface vibrations perpendicular to the surface.

A second low energy loss is observed at 36 meV when the clean crystal is cooled to 78 K. The surface has $c(2\times2)$ symmetry which can couple surface phonon modes from $\bar{M}$ and $\bar{\Gamma}$ and allow them to be observed in specular scattering geometry. Similar coupling due to ordered adsorbate structures has been observed on Ni(111).[10] The mapping of $p(1\times1)$ $\bar{M}$ and $\bar{\Gamma}$ in the $c(2\times2)$ surface Brillouin zone is shown in Fig. 1. The observed vibrational energy is above the bulk phonon maximum, indicating that the surface phonon band from $\bar{\Gamma}$ to $\bar{M}$ lies above the bulk continuum. An increase in the surface force constants can cause the surface band to lie above the bulk bands. Phonon band calculations must also include new lattice sums due to the reconstructed surface.

Figure 1 also shows a room temperature spectrum for clean W(100). Small features near 70, 110, and 155 meV result from low coverage CO, deuterium, and hydrogen adsorbed from the background pressure of $2\times10^{-11}$ Torr. There are no losses observed below 45 meV. This result suggests that the clean room temperature surface is disordered, and therefore, cannot support the bulk phonon mode resonance since the required symmetry is destroyed.

Low coverage hydrogen spectra have not shown any clear low energy features. This is partly due to long signal averaging times needed for the high resolution EEL spectra. The low coverage hydrogen surface is known to be a dynamic surface,[4] as the structure changes from commensurate $c(2\times2)$ to incommensurate $c(2\times2)$ to disordered surface as hydrogen coverage increases. Very careful LEED work

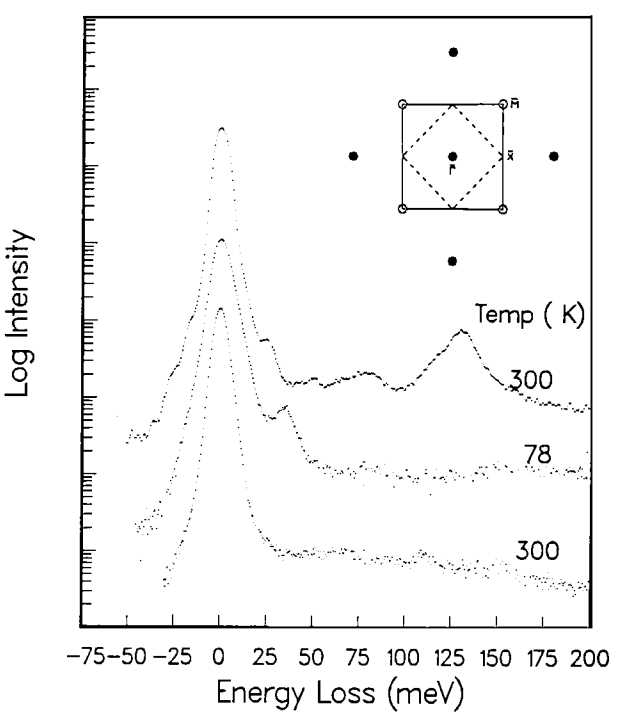


FIG. 1. Specular (60°) EEL spectra for hydrogen saturated surface $E_{inc}$ = 3.9 eV (upper spectra), clean cooled surface $E_{inc}$ = 4.5 eV (middle spectra), and clean room temperature surface $E_{inc}$ = 4.2 eV (lower spectra). Insert: Two-dimensional LEED spots and Brillouin zones; $p(1\times1)$ solid circles and solid line, $c(2\times2)$ open circles and dotted line.

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will be required in conjunction with single sweep, low signal-to-noise ratio EELS experiments to study the ordered low coverage hydrogen states.

In summary, high resolution EELS has yielded strong evidence for the disorder–order transition of the W(100) surface. Two distinct low energy loss peaks have been observed and attributed to independent loss mechanisms involving (1) bulk phonon vibrations from the commensurate surface and (2) surface phonon vibrations from the Brillouin zone edge mapped back to the zone center by the reconstructed surface layer. The clean room temperature surface exhibits no phonon modes. This can be attributed to the loss of long range order at the surface.

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# Summary Abstract: The lattice parameter of metallic monolayers

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Interest in thin metal overlayers on various substrates has led to a variety of studies on the behavior of metallic monolayers on surfaces.[1,2] A number of these experimental studies have reported growth of metallic layers on strongly chemisorbing substrates with some general rules developed for epitaxial growth.[3] The recent advent of self-consistent total energy calculations has, in addition, opened up the possibility of theoretically describing the atomic structure of unsupported monolayer films with interests in predicting epitaxial growth.[4,5] Calculations have been made for cesium and aluminum films, but have been compared to data for strongly chemisorbed systems, e.g., Cs on tungsten.[6] Our past interest in single crystal graphite and its inert properties has led us to look at the structural behavior of monolayer films of Li, K, Cs, and Al on graphite for the express purpose of defining the extent of monolayer lattice relaxation in metal films.

The adsorption experiments were performed in an ultrahigh vacuum chamber equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and a crystal manipulator with the capacity for cooling the sample to 20 K and heating to 1800 K.[7] The graphite substrate was naturally occurring single crystal graphite which was cleaved to expose the (0001) surface by the high-pressure nitrogen gas method.[8] This resulted in an extremely low surface step density reducing any possible effects of steps on the metal monolayer's behavior. Li, K, and Cs were evaporated from shuttered and calibrated thermal getter sources and the Al was evaporated from a small shuttered tungsten boat.

The observations of interest were the interatomic spacing for the metal atoms in metallic or psuedometallic monolayer form on the graphite surface. These were obtained from LEED diffraction patterns by direct comparison of adsorbate diffraction spot separations (and symmetries) with substrate graphite diffraction spots. It was assumed that the overlayer diffraction spots were the result of scattering from an overlayer for which there was a single adatom per overlayer lattice point. This allowed for overlayer interatomic distance measurements which did not require full dynamical calculations.

Exposure of graphite to potassium resulted, under an exposure equivalent to about 1 monolayer coverage, in a $\sqrt{3}\times\sqrt{3}$-R30° superstructure. This structure in the simple structural model would require a K–K distance in the overlayer of 4.26 Å. The K–K distance in bulk bcc potassium is 4.62 Å. Hence, what we are observing is an $\sim 8\%$ decrease in K interatomic spacing in a close-packed pseudometallic (as it is commensurate with respect to the graphite substrate) monolayer of potassium on graphite. This is consistent with the above noted theoretical expectation of lattice contraction in monolayer films.[5,6]

Cesium evaporation onto graphite at an exposure equal to about a full monolayer coverage also resulted in a $\sqrt{3}\times\sqrt{3}$-R30° superstructure. However, this was accompanied by a sharp, though weak, ring through the $\sqrt{3}$ spots. The $\sqrt{3}$ structure implies a Cs–Cs spacing of 4.26 Å in the overlayer. This is about 19% less than found in metallic bcc Cs (5.24 Å). In addition, the ring structure indicates that the Cs is losing registry with the graphite but still retaining the $\sim$4.26 Å Cs–Cs spacing. This points to a weakening of the Cs–graphite interaction reflecting the inert nature of the graphite and making comparison to calculated interatomic spacings for unsupported Cs films[6] more appropriate.

Additional exposure of the $\sqrt{3}\times\sqrt{3}$-R30° Cs structure to cesium resulted in a diffraction pattern consistent with the formation of a (100) bcc Cs surface. This is observed at an additional Cs exposure which equates to a total coverage of $\sim$2 monolayers, and for this approximately 2 layer thick bcc film on graphite a $4\% \pm 2\%$ decrease in intralayer lattice

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