

the intensity of the central peaks without some knowledge of the mosaic spread of the ω -phase material.

Experiments to investigate the detailed structure and temperature dependence of the anomalies observed in bcc Zr, in particular at N and $\frac{2}{3}[111]$ as well as the elastic peaks in the vicinity of the reciprocal lattice points of the ω phase on high-purity samples, are presently in progress at the HFIR of the Oak Ridge National Laboratory. We are also planning to investigate whether the phonons of the $L[111]$ branch exhibit deviations from cubic symmetry as observed by Axe *et al.*⁴ in their study of bcc Zr-Nb alloys.

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Hydrogen-Adsorption-Induced Reconstruction of Tungsten (100): Observation of Surface Vibrational Modes

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The surface vibrational modes of atomic hydrogen adsorbed on W(100), observed by electron-energy-loss spectroscopy in off-specular directions, indicate bridge bonding at all coverages. The vibrational frequencies show a dependence on the W-H-W bond angle which changes due to reconstruction of the tungsten lattice. The results indicate a W(100) $c[2 \times 2]H$ low-coverage β_2 phase consisting of atoms occupying bridge sites on a $(\sqrt{2} \times \sqrt{2})R 45^\circ$ reconstructed substrate similar to the clean crystal surface at low temperatures.

Low-energy electron-diffraction (LEED) studies of the chemisorption of hydrogen on the (100) face of tungsten show a complex series of changes occurring with increasing coverage. Previous discussions¹ attempted to explain the observations in terms of structural models in which the hydrogen atoms were located at various adsorption sites on an *undistorted* substrate surface. However, whereas the observations are consistent

with H occupying nearest-neighbor bridge-bonding sites W-H-W to form a (1×1) superstructure on the unreconstructed surface at saturation coverage ($\beta_1 \approx 17 \times 10^{14}$ H atoms/cm²), LEED intensity calculations² were found to be incompatible with all structures proposed to date to explain low-coverage adsorption.

The reason would appear to relate to the fact that the clean tungsten surface is unstable at

room temperature and reconstructs. In particular, the W(100) $c[2 \times 2]H$ structure obtained at a coverage, $\beta_2 \approx 0.25\beta_1$ (or $\sim 4 \times 10^{14}$ H atoms/cm²), produces LEED intensity spectra very similar to those from the $c(2 \times 2)$ reconstructed surface formed by low-temperature cooling of the clean crystal.³⁻⁵ This has led to the suggestion² that the two structures are closely related and the $c(2 \times 2)H$ layer derives from the periodic lateral displacement of the W atoms within the plane of the surface along the $\langle 11 \rangle$ direction of wavelength $\sqrt{2}a$ (lattice parameter $a \approx 3.16$ Å), proposed by Debe and King⁵ for the clean W(100) surface. The hydrogen effectively plays an impurity stabilizing role in a soft-phonon-mode-induced mechanism⁶ such that the W(100) $c[2 \times 2]H$ superstructure relates to the reconstructed substrate surface.

In this paper, we demonstrate that this is indeed the case. The method which we have used monitors the vibrational modes relating to the adsorbed H atoms by inelastic electron-energy-loss spectroscopy (ELS).⁷⁻⁹ These modes are shown to be sensitive to the lateral movement of the W atoms such that any adsorbate-induced reconstruction of the substrate surface can be observed as a function of coverage.

The angular dependence of the relative intensities of the W(100) $c[2 \times 2]H$ vibrational losses is shown in Fig. 1. As demonstrated in an earlier publication,⁷ the number of observed modes relates to the point-group symmetry of the adsorption site and vibrational motion lateral as well as perpendicular to the surface may be observed at angles off the specular beam direction. For the saturated $(1 \times 1)H$ bridge-bonded structure,⁷ the C_{2v} -symmetry point group gives rise to three non-degenerate vibrational modes: a symmetric stretch motion normal to the surface ($h\nu_1 \approx 130$ meV) and two lateral vibrations ($h\nu_2 \approx 80$ meV and $h\nu_3 \approx 160$ meV) corresponding to motion perpendicular and in the plane of the W-H-W bridge bond. The fact that three fundamental modes ($h\nu_1 \approx 155$ meV, $h\nu_2 \approx 60$ meV, and $h\nu_3 \approx 125$ meV), together with weak overtones of the most intense losses, are also observed for the W(100) $c[2 \times 2]H$ β_2 -phase coverage ($\Delta\theta_s \neq 0^\circ$, Fig. 1) indicates bridge bonding between two substrate W atoms rather than H-atom adsorption directly on top of a W atom (single coordination) as proposed in earlier ELS studies of this phase^{8,9}; the ν_2 and ν_3 lateral modes would be degenerate for on-top bonding. The dipole moment normal to the surface associated with the ν_1 (symmetric stretching) mode produces the intense energy-loss peak

observed in the specular direction.⁸ However, in off-specular directions the lateral vibrational modes, ν_2 and ν_3 appear with increasing relative

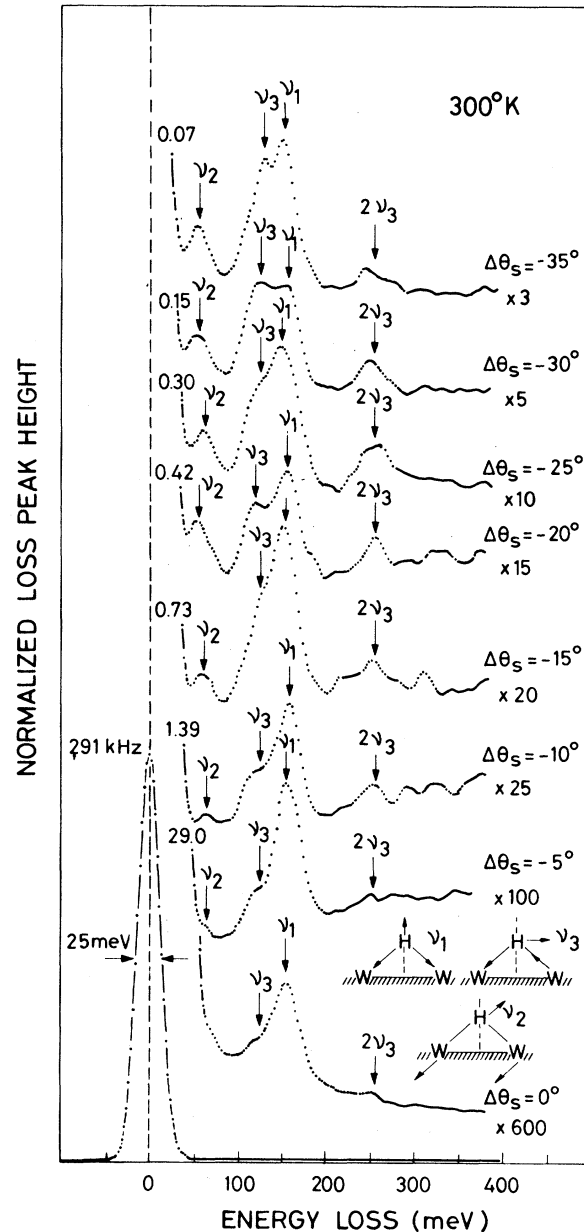


FIG. 1. Angle dependence of the normalized electron-energy-loss spectra as a function of the scattering angle $-\Delta\theta_s$ off the specular direction towards the surface normal in the $[100]$ plane of incidence for the W(100) $c[2 \times 2]H$ (β_2 phase) overlayer. The elastic beam count rate (in kilohertz) is indicated for each curve, impact energy $E_p = 5.5$ eV, energy resolution $\Delta E_p \approx 25$ meV, and incident angle $\theta_i = 60^\circ$. The frequencies of the fundamental vibration modes (inset), corresponding to bridge-site C_{2v} -symmetry bonding, depend on the W-H-W bond angle.

intensity. Much weaker energy-loss structure around $2\nu_3 \approx 250$ meV can be associated with overtone and combination bands of the three fundamental modes appearing at lower energies. This off-specular behavior identifies the ν_2 and ν_3 modes as lateral modes.⁷

In addition, the present work establishes the important fact that the frequencies of the observed modes are sensitive to the W-H-W bond angle¹⁰⁻¹² and, hence, to the lateral spacing of the W atoms. In particular, the ν_1 (symmetric stretch) and the ν_3 (asymmetric stretch) frequencies should switch over when the bond angle becomes less than about 90° , and the out-of-plane bending mode frequency ν_2 should soften considerably.¹² The present results (Fig. 1) show this to be the case, the frequencies of the ν_2 and ν_3 modes being much lower than is observed for the $(1 \times 1)\text{H}$ structure,⁷ suggesting that the W atoms move closer together at the lower coverage.

The question of the possible magnitude of the required atomic shift is illustrated with reference to the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface structure of the reconstructed substate lattice, Fig. 2(a). This model⁵ involves atomic shifts parallel to the plane of the surface along the $\langle 11 \rangle$ direction, as indicated in Fig. 2(a), and more clearly in Fig. 2(c). The wavelength of this periodic lattice distortion is $\sqrt{2}a$ (a = lattice spacing) and it is tentatively proposed that the H atoms occupy the bridge sites shown (black dots) in the $\text{W}(100) c[2 \times 2]\text{H}$ superstructure. This means that the W atoms move closer together in the reconstructed surface, the lattice spacing decreasing from a to a' [Fig. 2(b)]. Assuming a constant W-H bond length of $1.95 \pm 0.05 \text{ \AA}$,¹³ the W-H-W bond angle for the unreconstructed surface $2\alpha \approx 108^\circ \pm 5^\circ$ corresponding to a height above the surface of $1.15 \pm 0.05 \text{ \AA}$. For this angle to decrease to or below 90° , the lattice spacing must decrease to a value $a' \approx 2.76 \text{ \AA}$ giving a displacement $|\vec{d}| \approx 0.30 \pm 0.05 \text{ \AA}$, in good agreement with recent estimates based on LEED calculations for the clean reconstructed surface² ($0.15 \leq |d| \leq 0.3 \text{ \AA}$) and ion-channeling experiments on the $c(2 \times 2)\text{H}$ structure ($|d| > 0.2 \text{ \AA}$).¹⁴ This value is also close to the nearest-neighbor bulk lattice spacing ($a' = 2.74 \text{ \AA}$) which would give $|\vec{d}| \approx 0.32 \text{ \AA}$ and a W-H-W bond angle, $2\alpha = 89^\circ$, for the reconstructed surface. For comparison, if we assume a W-H bond length based on unrealistic W-H Pauling radii of 1.62 \AA , $2\alpha \approx 154^\circ$ for the unreconstructed surface, requiring a shift of $|\vec{d}| \approx 0.8 \text{ \AA}$ [i.e., $a' \approx 2.3 \text{ \AA}$, Fig. 2(c)] to reduce the W-H-W bond angle $2\alpha \approx 90^\circ$; such a

shift is unacceptably large on the basis of the LEED² and ion channeling¹⁴ measurements. It would also be difficult to reconcile the present

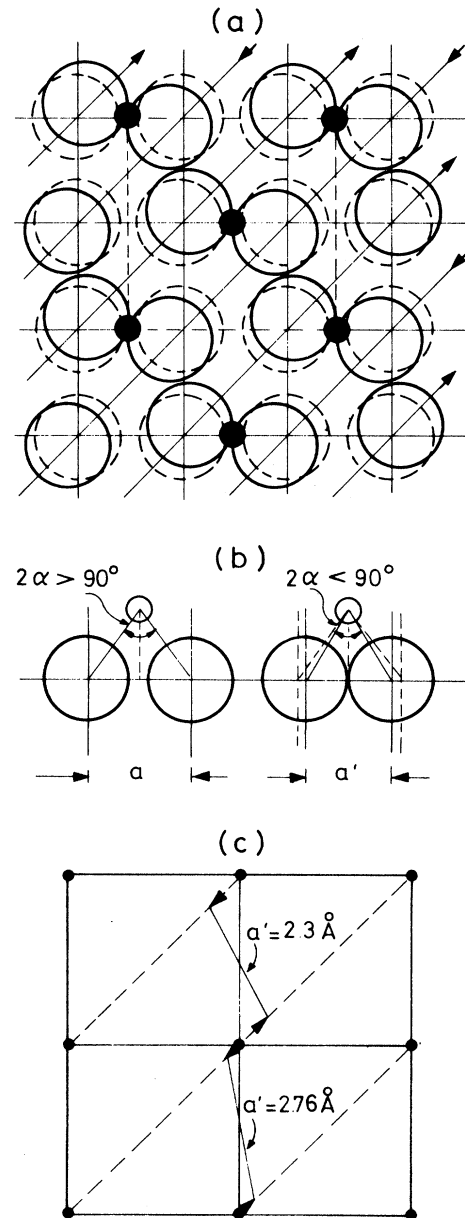


FIG. 2. Surface reconstructed-layer model for $\text{W}(100) c[2 \times 2]\text{H}$ showing (a) the bridge-site positions of the chemisorbed H atoms (small circles) between two W atoms before (dashed large circles) and after (full-line large circles) reconstruction; the $c(2 \times 2)\text{H}$ unit mesh (dashed-line square) and the direction of the W-atomic shifts (arrows) are indicated; (b) the change in the W-H-W bond angle, 2α ; and (c) the magnitude of the W-atomic displacements, required to produce a decrease in the lattice spacing, $a \approx 3.16 \text{ \AA}$, to the values a' shown.

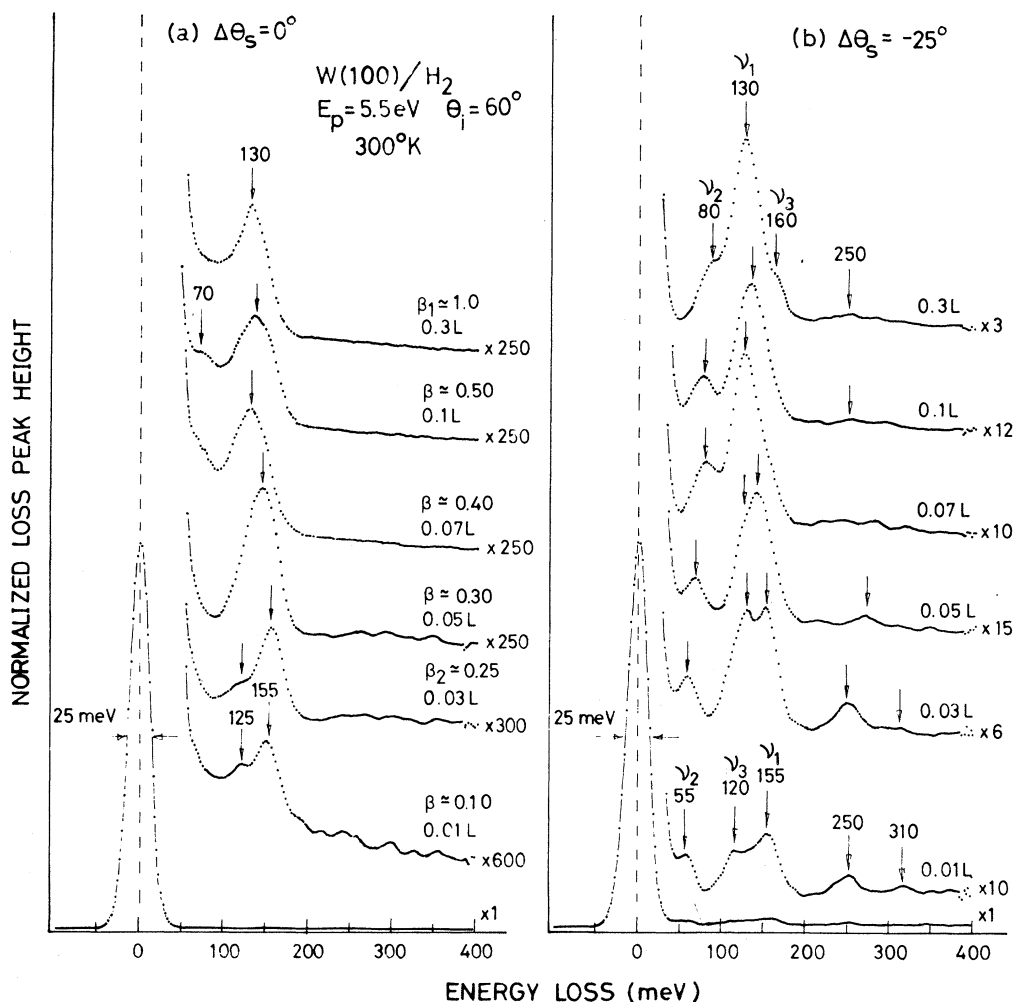


FIG. 3. Coverage dependence of the normalized electron-energy-loss spectra: (a) in the specular beam direction; (b) -25° off-specular towards the surface normal. The surface coverage β is indicated as a fraction of that at saturation coverage $\beta=1$ and an exposure to H_2 gas in langmuirs ($1 L=10^{-6}$ Torr sec). The approximate coverages corresponding to the $c(2 \times 2)H$ (β_2 phase) and the $(1 \times 1)H$ (β_1 phase) overlayer structures are indicated.

angle- and coverage-dependent ELS measurements with such a large shift.¹⁵

The coverage dependence of the ELS spectra is shown in Fig. 3. The gradual shift of the low-energy bending mode $h\nu_2=55$ to 80 meV [Fig. 3(b)] with increasing coverage (referring to saturation coverage $\beta_1=1$), is a clear indication of a second-order phase transition^{2,4} in which the displaced W atoms revert back to their bulk lattice positions [dashed circles, Fig. 2(a)]. The associated complex switching of the positions of the energy-loss features associated with the lateral (ν_3) and perpendicular (ν_1) bridge-site stretching modes is clearly apparent in the off-specular scattering direction [$-\Delta\theta_s=25^\circ$, Fig. 3(b)]. This reconstruction of the $(\sqrt{2} \times \sqrt{2})R45^\circ$ structure back

to a (1×1) surface is also the reason the single intense loss observed in the specular direction ($\Delta\theta_s=0^\circ$) at $h\nu_1=155$ meV for the $c(2 \times 2)H$ phase decreases to $h\nu_1=130$ meV at saturation coverage [Fig. 3(a)] rather than a transition from adsorption sites on top of the W atoms to bridge sites proposed in earlier work.^{8,9} Similar behavior has been observed for adsorption at $100^\circ K$.^{2,16}

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¹⁵Weak intensity corresponding to the ν_2 and ν_3 modes is also observed in the specular direction (Figs. 1 and 3) which is indicative that these modes may have some normal-to-the-surface component, such as would be produced by a slight puckering of the tungsten substrate lattice.

¹⁶Subtle differences between the behavior at 100 and 300°K are seen, however, at very low coverages, below that required for the $c(2 \times 2)H\beta_2$ phase (M. R. Barnes and R. F. Willis, to be published).

Ballistic-Phonon-Pulse Transmission through a Solid-Liquid He II Interface at $T=0.25$ K

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The transmission of ballistic longitudinal (L) and transverse (T) phonon pulses from sapphire to liquid He II at temperatures of $T=0.25$ K has been measured as a function of the pulse power and He II hydrostatic pressure for the first time. Under these experimental conditions, the converted L- and T-mode pulses propagate ballistically through He II. The results indicate that the transmission probability is different for the L and T modes and that the intensity ratio of converted L and T modes changes with the He II pressure.

The transmission of phonon energy through solid He II interfaces has attracted a great deal of theoretical and experimental interest in recent years.^{1,2} Despite many very interesting findings³ and the use of new phonon-pulse techniques,⁴ the problem still evades solution. Because of the existence of phonon focusing in anisotropic solids,⁵ the interpretation of the more simple and most common reflection experiments is not unambiguous⁶ and energy-transmission experiments are needed. However, in the phonon-pulse transmission experiments performed up to now, either the time resolution was too low to resolve converted longitudinal (L) and transverse (T) modes,⁷ or the temperature of He II was so high ($T \approx 1.5$ K) that the phonon-roton interaction was intense and the energy transport from the interface oc-

curred in a collective mode (second sound) resulting in a very small phonon mean free path.⁸ In this paper, we report on the first observation of the direct conversion of L- and T-polarized phonon pulses from a solid into well-resolved ballistic-phonon pulses in liquid He II. The experimental conditions (He II temperature $T=0.23$ K, hydrostatic pressure $p=24$ bar) are such that, as a result of the normal (downward) dispersion relation of He II, the phonon mean free path l in He II is macroscopic ($l > 1$ mm).⁹ The conversion of L and T phonon modes at the solid-liquid interface can therefore be studied in a direct way.

In the present experiment, fast-heat-pulse techniques at very low temperatures are used for the time resolution of the converted L and T modes. Our measurements indicate a changed ratio of