Anomalous Thermal Expansion of Ni(001)

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We show that the high-temperature Ni(001) surface undergoes a large vertical expansion. LEED experiments indicate that the surface thermal-expansion coefficient α_{surf} increases rapidly between 900 and 1300 K, reaching a value nearly 20 times larger than in the bulk. These results directly confirm that a large anharmonicity in the interatomic potential develops on metal surfaces and that it may be a precursor to various surface disordering transitions.

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Solid surfaces become unstable to the formation of topological defects at high temperatures and transform to disordered phases. Two such phase transitions, surface roughening and surface melting, have been intensively studied on (110) fcc metal surfaces. Surface roughening, the formation of steps leading to vertical disorder, has been observed on the $(11m)$ facets of Cu[1] and Ni[2] and on (110) Pb,[3] Ni,[4] and Pt.[5] Surface melting, the loss of lateral order, has been observed on Al(110)[6] and on Pb(110).[7] In the case of Pb(110) the melting was preceded by a roughening transition.[3] In spite of the work to date, several important questions concerning the stability of crystal surfaces remain. Why do some surfaces roughen and others melt; i.e., what are the forces that drive these transitions? Is surface melting a general phenomena or is the transition only confined to high-Miller-index surfaces? It is these questions that have motivated this study of the high-temperature structure of the Ni(001) surface.

Unlike the (110) surfaces, there are few studies of the high-temperature structures of low-index surfaces. Au(001) is the notable exception, having a low-temperature incommensurate distorted hexagonal phase.[8] Above 1170 K the incommensurate surface layer loses lateral order.[8] An anomalous narrowing of LEED profiles from Pb(111) also suggests that an initially roughened surface may melt above 580 K but the exact structure of the high-temperature phase is still not completely known.[9] It is also interesting to speculate how an anharmonicity in the surface interatomic potential affects the high-temperature stability of surfaces. Measurements suggest that the roughening transitions on (110) and $(11m)$ Ni and Cu surfaces are preceded by an enhanced atomic vibrational amplitude.[1,2,4] Helium-scattering experiments also indicate that a large anharmonicity is present on Ni(001),[10] raising the following question: Will this surface also disorder at high temperatures?

We report high-q-resolution LEED experiments on Ni(001). We will show that the surface thermal-expansion coefficient α_{surf} increases to $> 20\alpha_{bulk}$. In a later paper we will also show that, subsequent to the vertical expansion, the surface develops lateral disorder near 1300 K without the formation of steps.[11]

The experiments were carried out in a UHV chamber (base pressure $< 8 \times 10^{-11}$ Torr). The LEED system consists of a low-divergence electron gun, Faraday cup, and five-circle diffractometer. The system has a transfer width of 4800 Å at a momentum transfer of 2.5 Å^{-1}.[12] A 10-mm-o.d.×2.5-mm-thick Ni(001) crystal was oriented, mechanically polished, and electroetched. Temperatures were measured with a Chromel-Alumel thermocouple that was checked against an optical pyrometer calibrated to the gold melting point. The sample temperature can be stabilized to within ± 0.5 K with an absolute accuracy of ± 25 K.

The major surface impurities were carbon, oxygen, and sulfur as determined by Auger electron spectroscopy (AES). The cleaning process included 10^{-7}-Torr oxygen exposure at 670 K to eliminate carbon, followed by 40 h of 500-eV argon sputtering at 1300 K to remove the excess oxygen and sulfur. Although no impurities were found on the surface by AES, the diffraction peaks showed a splitting ($\Delta q \sim 0.03$ Å^{-1}), indicating a large-scale surface reconstruction. The physical origin of the reconstruction is unknown. We believe that trace amounts of sulfur diffusing from the bulk at 1300 K were responsible for the reconstruction. The superlattice peaks disappeared after more than 80 h of high-temperature sputtering followed by annealing from 1300 to 670 K at a rate of 0.25 K/sec.

The cleanness and order of the sample were characterized by a sharp, in-phase diffraction peak with a full width at half maximum that remained constant throughout the heating and cooling process. The major contribution to the finite diffraction-peak width was the sample mosaic, which is $< 0.15°$. This mosaic angle places a lower limit of 700 Å on the finite sample size. In this paper the momentum transfer Q is always given in units of the conventional bulk cubic reciprocal lattice, $(1.78$ Å$^{-1})(h,k,l)$.

Previous studies of Ni(110)[4] and Cu(110)[13] indicate that these surfaces may have a large anharmonic interatomic potential. We have also observed evidence for a

similarly large anharmonicity on Ni(001). In the previous studies, as well as those reported here, the anharmonicity is inferred from the temperature dependence of the diffraction-peak intensities, $I(T)$.[4,13] In the Debye-Waller model $I(T)$ is given by

$$\ln(I/I_0) = -\langle [\mathbf{Q} \cdot \mathbf{u}(T)]^2 \rangle, \qquad (1)$$

where I_0 is the diffraction intensity at $T = 0$ K. The mean-squared vibrational amplitude $\langle u_H^2 \rangle$ is proportional to T in the harmonic approximation. Measured deviations of $\ln(I_{\text{peak}})$ from a linear temperature dependence are interpreted as being due to an anharmonic potential, leading to T^2 and T^3 terms in $\langle u^2 \rangle$. Figure 1 shows normalized intensity data versus temperature for several surface diffraction peaks. The linear Debye-Waller term, $I = I_0 \exp(-Q^2 \beta T)$, has been divided out of the data to clearly show the nonlinear behavior. $\beta = \langle u_H^2 \rangle / T$ is a constant determined from data taken below 900 K where the data are still consistent with the harmonic model. As seen, significant deviations from a harmonic $\langle u^2 \rangle$ occur at 900 K, the same temperature as observed on Ni(110).[4]

A direct consequence of an anharmonic potential should be an enhanced surface thermal-expansion coefficient α_{surf}. While a lateral surface expansion cannot be measured [unless the top layer becomes incommensurate with the bulk, which has not been observed for Ni(001)], it should be possible to determine the vertical thermal expansion. In a kinematic scattering model the energy position of peak in the intensity versus voltage (I-V)

profile of a diffraction rod is proportional to $d^{-1/2}$, where d is the vertical layer spacing. Figure 2 shows the specular I-V profile near the (002) position for two sample temperatures. At higher temperatures the position of the peak shifts towards lower energies, consistent with an outward expansion of the surface atoms. While an exact determination of the expansion requires a full dynamic LEED calculation, including multiple scattering and a layer-dependent vertical expansion, we can estimate α_{surf} using the definition

$$\alpha_{\text{surf}} = -\frac{1}{2} \frac{\partial \ln(E_{\text{peak}})}{\partial T}. \qquad (2)$$

We have plotted $\ln(E/E_0)$ (where E_0 is the position of a peak in the I-V profile at $T = 300$ K) as a function of temperature in Fig. 3. Note that the energy shifts of three different peaks, two near the (002) position [labeled (1) and (2) in Fig. 2] and a third near the (004) position, are all equal to within experimental error. This result supports the assertion that multiple-scattering effects are not too important in these relative peak-shift measurements. If they were, we would expect that the different scattering geometries [$\theta_i = 73.5°$ and 45° for the (002) and (004) data, respectively] would produce different temperature-dependent energy shifts. Though multiple-scattering effects and a z-dependent α must be present, their contributions evidently lie outside the experimental sensitivity.

We can offer a crude estimate for the depth of the expansion. The width of a peak in the I-V profile is roughly given by $\Delta d / d = \Delta E / 2E$, where Δd is the thickness of the coherently scattering selvedge. From an average of several I-V peaks Δd is approximately 20 Å. This should be an overestimate since the elastic mean free path is only ~ 3 Å at the energies in these experiments.[14]

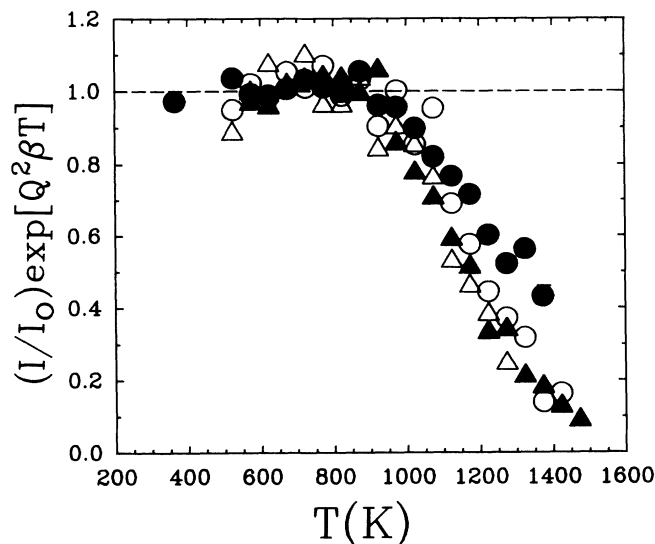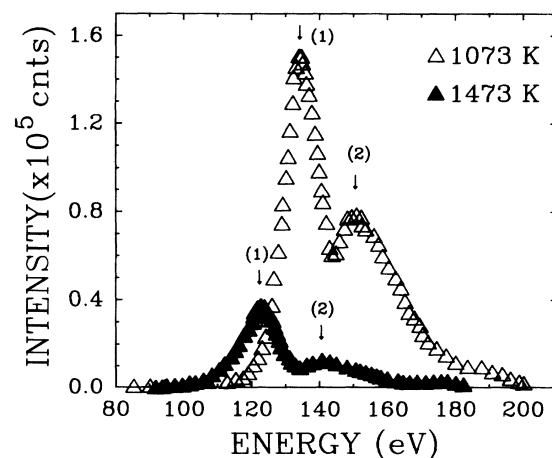α_{surf} was calculated by first averaging the tem-

FIG. 1. $I(T)$ vs T data for Ni(001). Data have been normalized to the harmonic Debye-Waller factor as described in the text. Data are for four reflections: ●, (003), $E = 156.8$ eV, $\theta_i = 65.4°$; ▲, (004), $E = 157.4$ eV, $\theta_i = 56.4°$; ○, (113), $E = 80$ eV, $\theta_i = 37.3°$; △, (204), $E = 150$ eV, $\theta_i = 24.1°$. Dashed line would be the T dependence for a harmonic theory.

FIG. 2. LEED I-V profiles of the specular rod $(0,0,l)$ near the (002) position for two sample temperatures. The incident angle, with respect to the sample normal, is 73.5°.
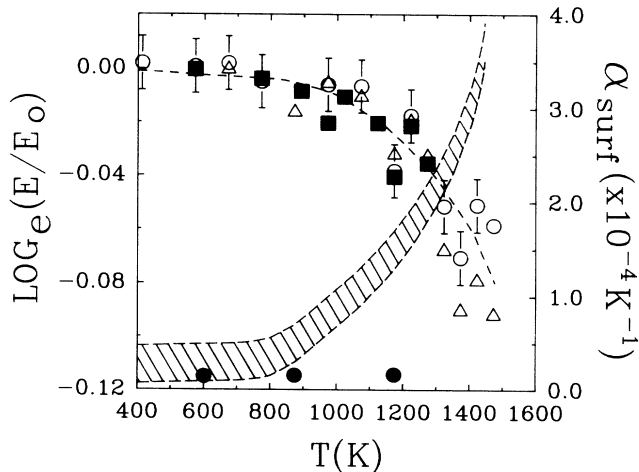
FIG. 3. The natural logarithm of the I-V energy shifts, normalized to the $T=300$ K peak position vs temperature. Data are shown for $E_0=136$ eV, $\theta_i=73.5°$ ($\triangle$); $E_0=150$ eV, $\theta_i=73.5°$ ($\circ$); and $E_0=150$ eV, $\theta_i=45°$ ($\blacksquare$). Dashed line is the average energy shift. α_{surf} vs temperature is bounded by the shaded region. $\bullet$, α_{bulk} (Ref. 15).

perature-dependent energy shifts of the three I-V peaks described above (the dashed curve in Fig. 3). The average shift was then used to determine α_{surf} (the shaded region in Fig. 3 reflects the uncertainty in determining α by this method). Below 900 K, α_{surf} is consistent with the bulk value ($\alpha_{bulk}=1.63\times10^{-5}$ K^{-1} at 1173 K)[15] as indicated in Fig. 3. Above 900 K, α_{surf} starts to increase dramatically, approximately the same temperature that the diffraction intensities deviate from a harmonic Debye-Waller model. By 1350 K, α_{surf} is about 20 times larger than the bulk value. For reference, the peak energy shift corresponds to a $\sim 3\%$ increase of the vertical interlayer spacing from 300 to 1300 K.

The correspondence between α and the diffraction-peak decay indicates that the temperature dependence of $I(T)$ is thermal in origin and not due to any structural transition or disorder. It further supports claims that similar intensity behaviors on Cu(110) and Ni(110) are not due to defect formation.[4,13]

A caveat of the I-V peak shift is that it influences the temperature dependence of LEED intensities. Any intrinsic temperature dependence, from atomic vibrations or a structural transition, for instance, will be modulated by temperature-dependent shifts of the I-V profiles. This is particularly true if data are taken at a peak in the I-V profile where even small energy shifts can dramatically change the collected electron current. Therefore, quantitative information based on $I(T)$ alone must be treated with caution.

Recently, Prince, Breuer, and Bonzel[16] reported that Pb(110) underwent an asymmetric surface melting transition. This conclusion was based on a different temperature dependence for the Pb(110) (10) and (01) LEED rods. The observed differences may in fact be simply due

to different I-V shifts on the two rods. Further experiments will be necessary to determine which assertion is correct.

An interesting observation can be made by comparing this work with similar studies on Ni(110). Both the Ni (001) and (110) surfaces have a large anharmonic surface potential that is clearly evident above 900 K. This confirms theoretical predictions. Using Morse-type potentials, Jayanthi and Tosatti[17] calculated the quasiharmonic free energy and showed that a vibrational instability should occur at approximately the same temperature on both (110) and (001) fcc surfaces. The implication of a larger surface anharmonicity, compared to the bulk, is that a stress must build up in the surface. While these two surfaces are similar in that respect, the isotropies of the vibrations are quite different. On Ni(110) the vibrations were found to be isotropic in the surface but the amplitudes parallel to the surface were much larger than the perpendicular vibrations.[4] This anisotropy has also been observed in simulation studies of Ni(110) using embedded-atom potentials.[18] In contrast, we find that the atomic vibrations on the Ni(001) surface (measured below 900 K) are isotropic parallel and perpendicular to the surface; $\langle u_\parallel^2\rangle/T=\langle u_\perp^2\rangle/T\approx 4\times10^{-5}$ Å^{2}K^{-1}. These values are about 30% higher than $\langle u_\perp^2\rangle/T$ measured for Ni(110).[4]

These differences suggest that the more open (110) surface has a "stiffer" holding potential to the substrate compared to the in-plane bonds, forcing the bulk parallel periodicity on the surface atoms. At higher temperatures the stress may be more easily taken up on the (110) surface by increasing the step density, which preserves the lateral periodicity. The rough (110) surface would have a lower average atomic density per plane leading to a smaller s-electron kinetic-energy term. It may be that the s-electron pressure, which is known to drive (2×1) missing-row reconstructions on Ir, Pt, and Au(110),[19] is the origin of the stress on this surface.

For Ni(001) the situation is quite different. The symmetry of the vibrations implies that the bonding strengths in plane and out of plane are nearly equal. This suggests that the surface stress is nearly isotropic. At higher temperatures, as the stress builds, the thermal expansion applies an outward pressure normal to the surface, overcoming the d-electron negative partial pressure.[20] The entire surface layer is lifted from the underlying bulk. Because the d-electron contribution to the bonding is short range, the larger vertical spacing in the top layers may signal a decreasing influence of the bulk periodicity on the top layers. Adatom-vacancy pairs are harder to generate on an (001) face because of the higher surface coordination compared to (110). Interstitials may be more easily formed in the top layer similar to the quasiliquids seen in simulations.[18] Diffraction data indicate that Ni(001) does remain flat (i.e., no steps form) up to at least 1470 K but begins to lose lateral order as low as 1300 K, consistent with this picture.[11]

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