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Approach to Thermal Roughening of Ni(110): A Study by High-Resolution Low-Energy Electron Diffraction

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We present high-q resolution low-energy electron diffraction results of the approach to thermal roughening of the Ni(110) surface. The process is found to occur in two reversible steps. At temperatures above 900 K vibrations become a significant fraction of the bond length and a large anharmonicity in the vibrational amplitude appears. A large asymmetry between in- and out-of-plane vibrations exists, causing the off-specular diffraction peaks to decay rapidly to zero. Finally, near 1200 K, a significant density of vacancies begins to form. Above 1300 K the surface roughens.

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Both surface roughening and surface melting have been the subject of intense interest in the past several years. This is especially true of studies of fcc metal (110) surfaces since they may be prototypical systems, showing both surface roughening and surface melting. Pb(110) has been shown to exhibit a surface melting transition,[1] with evidence of predisordering at lower temperatures.[2] Attempts to look for similar transitions on other (110) metals have led to mixed results. X-ray studies on Cu(110) reported roughening near 870 K, but later experiments indicated that, instead, the surface reversibly faceted.[3,4] Helium-atom scattering from Cu(110) indicated no evidence for any structural transition, instead suggesting that the temperature dependence of the diffraction intensity could be explained by a large anharmonic mean-square vibrational amplitude, $\langle u^2\rangle$.[5] The existence of a roughening transition on the structurally similar Ni(113) surface[6] has led to speculation that Ni(110) should roughen as well. We report high-resolution LEED results on Ni(110). We show that, like Cu(110), an anharmonicity develops in the Ni-Ni potential above 900 K but, in contrast, we find that Ni(110) has a roughening transition near 1300 K.

The experiments were carried out in UHV (1×10^{-10} Torr), using a newly developed high-resolution LEED system.[7] The system has a transfer width of ~4800 Å for a momentum transfer of 2.5 Å^{-1}. Samples were oriented and polished to ~0.2°. After polishing ~40 μm of surface material were removed by electropolishing in a 50% H_2SO_4 solution (0.5 A/cm^2). Excess subsurface carbon was removed by heating at 1120 K in a 2×10^{-6}-Torr O_2 atmosphere for approximately 24 h. Sputtering with 500-eV Ar^+ at a sample temperature of 1070 K removed any remaining O_2 and S. While the Auger showed no detectable contamination, the diffraction showed a nonreversible peak splitting when the sample was heated above 750 K. After three weeks of repeated sputtering at 1070 K followed by annealing the sample from 1170 to 670 K at a rate of 0.4 K/sec, no more splitting was observed and the sample was deemed clean and well ordered. The major contribution to the diffraction peak widths was the sample mosaic, $<0.16°$. An additional broadening at low momentum transfer was also observed and presumed to be the sample finite size. After deconvolving with the mosaic width, the finite domain size of the sample is estimated to be ~1400 Å. All of the data were taken by scanning the momentum transfer $Q_\parallel$ (parallel to the surface) keeping $Q_\perp$ (perpendicular to surface) fixed. This means that the incident angle, θ_i (relative to the sample normal), is scanned with only small corrections in the detector angle, θ_0 (relative to incident beam), needed to keep $Q_\perp$ constant. This method reduces asymmetries due to inelastic losses, atomic scattering factor, and the Lorentz factor.[8] Reciprocal-space points are labeled with respect to the conventional bulk cubic reciprocal-lattice vector, $\mathbf{a}^* = 1.785\ \text{Å}^{-1}(1,1,1)$.

We begin by presenting the diffraction intensity as a function of temperature. In order to clearly display the anomalous temperature behavior, we have qualitatively removed the effects of harmonic thermal vibrations by normalizing the experimental data using a kinematic Debye-Waller theory,[9]

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

where I_0 is the intensity at $T=0$ K, $\mathbf{Q}$ is the momentum transfer, and $\langle u^2\rangle$ is the mean-squared vibrational amplitude of an atom. In the harmonic model $\langle u^2\rangle \propto T$.[9] Of course, a quantitative analysis of the temperature dependence of the intensity requires inclusion of the attenuation of the electron beam. This in turn requires an assumed model for the decay of the vibrational amplitudes with depth from their surface values to their bulk values. Ignoring the finite penetration of the electron beam will underestimate the vibrational amplitude of the surface atoms since the diffraction intensity will be weighted more by subsurface layers.[10] To within a few percent, these effects will not alter the linear behavior of $\langle u^2\rangle$ as long as the potential remains harmonic.[10] For the purpose of further discussion we will use these values of $\langle u^2\rangle$ only as parameters to remove the normal Debye-Waller behavior of the scattered intensity. Indeed, up to 900 K, plots of $\ln(I)$ versus temperature are linear in temperature, consistent with Eq. (1). Within this temperature region, we find that perpendicular to the surface, $\langle u_\perp^2\rangle/T = 2.7\times10^{-5}$ Å^{2}K^{-1} (3 times larger than the bulk[11]). Vibrations parallel to the surface, $\langle u_\parallel^2\rangle$, are 5 times larger than $\langle u_\perp^2\rangle$ and are essentially isotropic in the surface plane. Specifically, $\langle u_\parallel^2\rangle/T = 1.5\times10^{-4}$ Å^{2}K^{-1} in the [001] direction and 1.7×10^{-4} Å^{2}K^{-1} in the [1$\bar{1}$0] direction.

Using these values of $\langle u^2\rangle$ we have normalized the data by dividing by $\exp(-2M)$. As seen in Fig. 1 the normalization adequately removes any temperature dependence up to 900 K, but at higher temperatures the deviations from simple harmonic vibrations are apparent. We find different temperature behaviors for the specular ($Q_\parallel = 0$) and off-specular ($Q_\parallel \neq 0$) rods. The specular reflections decay more slowly, independent of out-of-phase (110) or in-phase (220) scattering conditions. The off-specular peaks have a quite different behavior. Diffraction rods, in both the [001] ($\perp$ to the atom rows) and [1$\bar{1}$0] ($\parallel$ to the atom rows) directions, disappear rapidly above 900 K and are almost zero by 1200 K. Note that these data indicate that simple step formation, as in the case of a roughening transition, is not the cause of the intensity loss between 900 and 1200 K. Step formation would be indicated by a decrease in intensity of the out-of-phase peaks alone, with the in-phase peaks remaining unchanged.[12] Furthermore, no change in the diffraction line shapes is observed up to 1150 K; thus the loss of vertical or lateral order is not due to step formation.[12]

The sharp decrease in peak intensity above 900 K has been assigned to a large anharmonicity in the Ni-Ni potential for two reasons. First, no change in line shape has been observed for either specular or nonspecular diffraction peaks up to 1200 K, which would be associated with a disordering transition.[6,12] Second, vacancy formation can be ruled out, since no increase in the diffuse background is observed until 1100 K. Figure 2 shows the temperature dependence of the ratio of the background-to-peak intensity for two diffraction peaks. Note that even though the (420) peak intensity (Fig. 1) decreases rapidly above 900 K, the ratio remains linear up to 1150 K. This is consistent with one-phonon scattering as the source of the background (the one-phonon scattering intensity relative to the peak is $\propto T|Q|^2$).[10] Furthermore, the measured ratio is not large enough to account for the lost intensity. Assuming no relaxations, the background-to-peak ratio would be $n/(1-n)$ for a fraction of n vacancies per surface atom.[13] To explain the intensity decrease, the vacancy concentration would have to be ~30% at 1000 K. This predicts a ratio of about 0.4, compared to 0.04 measured at 1000 K in Fig. 2 (subtracting the thermal background would further lower the measured ratio).

These results are consistent with molecular-dynamics simulations (MDS). Using Morse-type potentials, an instability to large atomic vibrations has been predicted below the bulk melting temperature, T_m, for Cu(110).[14] These simulations show that the minimum in the quasiharmonic surface free energy, as a function of atomic separation, disappears between $0.76T_m$ and $0.97T_m$ (the higher value corresponding to the case

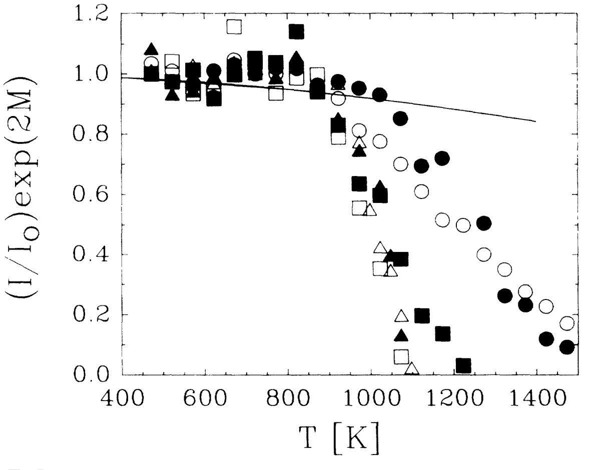

FIG. 1. Diffracted beam intensities vs T. The data have been normalized by a linear Debye-Waller factor. The specular peaks are (420 eV) (●) (110), $\theta_i = 83.1°$ and (○) (220), $\theta_i = 76.1°$. Off-specular peaks in the [001] direction (100 eV) (■) (332), $\theta_i = 60.6°$ and (□) (222), $\theta_i = 88.2°$, and in the [1$\bar{1}$0] direction (△) (420), $\theta_i = 48.0°$ and (▲) (310), $\theta_i = 78.6°$. Open and filled symbols are in- and out-of-phase conditions, respectively. The solid line is the intensity of the (220) peak due to bulk anharmonic vibrations (Ref. 11).

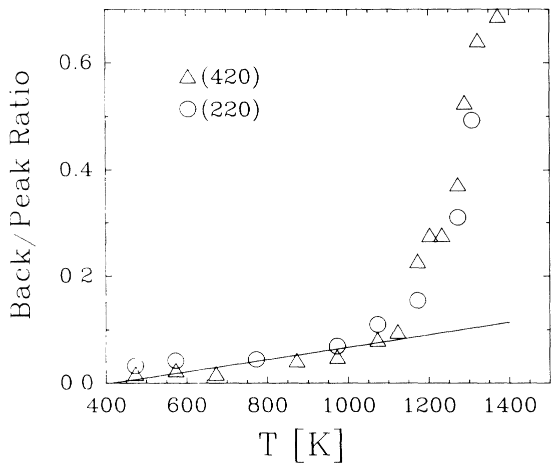

FIG. 2. The ratio of the background to peak intensity (measured 0.2 Å^{-1} away from the peak) vs T. The intensities have been normalized by $(Q/Q_{220})^2$. Data are shown for the reflections (△) (420) $E = 300$ eV, $\theta_0 = 126.6°$, and (○) (220) $E = 420$ eV, $\theta_0 = 152.2°$. The solid line is the predicted one-phonon background dependence.

where first-layer relaxations are included). Recent MDS on Cu and Ni(110), using effective-medium theory, also predict a large anharmonicity in the later vibrations.[15]

By 1150 K, the peak-to-background ratio sharply increases without a corresponding change in line shape, suggesting vacancy formation. The absolute vacancy concentration is difficult to measure because of multiphonon scattering, vacancy clustering, and strain fields associated with relaxations near the defects. However, after correcting for the thermal background, the concentration can be estimated to be between 5% and 15% at 1200 K (the error is primarily due to subtracting the quasielastic background). This type of increased vacancy density has been referred to as a quasiliquid because of the large lateral disorder associated with defect concentrations of ~20%.[16] The quasiliquid still maintains long-range order but is suggested to have a lateral correlation function similar to a low-density 2D liquid.[16] Attempts to look for a liquid scattering in this temperature region are under way.

Below 1200 K the out-of-phase line shape is characterized by a sharp, finite-size-limited, Gaussian central peak superimposed on a broad Lorentzian tail (see Fig. 3). The Lorentzian FWHM is about 0.077 Å^{-1} and is approximately isotropic in the surface plane. The simplest interpretation of this line shape is a two-level surface consisting of monoatomic steps, each step occurring independent of the other.[12] The Gaussian component has a width dependent only on the long-range order of the surface and subsurface regions. The Lorentzian intensity depends on $Q_\perp$, being maximum at the out-of-phase condition [i.e., $Q_\perp b = (2n+1)\pi$, where $b = 1.25$ Å is the step height on the (110) surface]. The width of the Lorentzian is proportional to the probability of making a step, while the ratio of the Gaussian to the Lorentzian intensity is directly proportional to the coverage of atoms in the top layer.[12]

Between 1200 and 1250 K the specular out-of-phase peaks begin to change. In this temperature range, the ratio of the Gaussian to the Lorentzian component begins to decay with no change in the Gaussian width (see Fig. 4). By 1400 K the Gaussian component has disappeared and the Lorentzian component has broadened considerably (see Fig. 3). The broadening is isotropic in the [001] and [1$\bar{1}$0] directions. The off-specular peaks have a similar behavior. A qualitative interpretation is found by considering the two-level model. Below 1200 K the coverage of top-layer atoms (calculated from the Gaussian-to-Lorentzian ratio and the Lorentzian width[12]) is constant, being 2.6% in any direction. Neglecting attenuation, the decrease in this ratio indicates that more atoms in the second layer are being promoted into top-layer positions. To do this, while conserving the total number of atoms, the probability to make a step must correspondingly increase. Thus, the Lorentzian tail must broaden. Up to the highest temperatures in these experiments, no change in the in-phase line shapes, $Q_\perp b = 2n\pi$, is observed for either specular or off-specular peaks. These observations are consistent with a roughening transition for $T \gtrsim 1300$ K.[6,17] On the other hand, they are inconsistent with a true liquid layer since such a layer would broaden the off-specular peaks as lateral order is lost.

The data suggest the anharmonicity as a possible driving mechanism for the roughening transition. Above 900 K an instability in the vibrational free energy occurs and the (110) surface becomes soft compared to the bulk. The relative anharmonicity between the surface and the bulk can be seen in Fig. 1, which shows the anharmonic contribution due to bulk variations. The thermal expan-

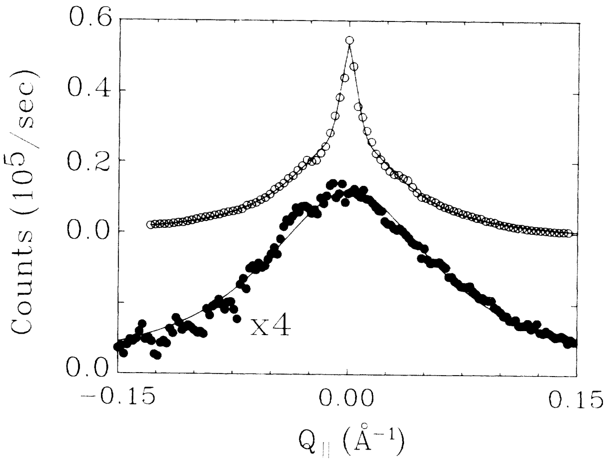

FIG. 3. Constant $Q_\perp = 2.52$ Å^{-1} scans across the (110) diffraction peak in the [1$\bar{1}$0] direction, $E = 420$ eV, $\theta_0 = 166.2°$. Data are for $T = 1373$ K (●) and $T = 723$ K (○). Solid curves are fits as described in the text.

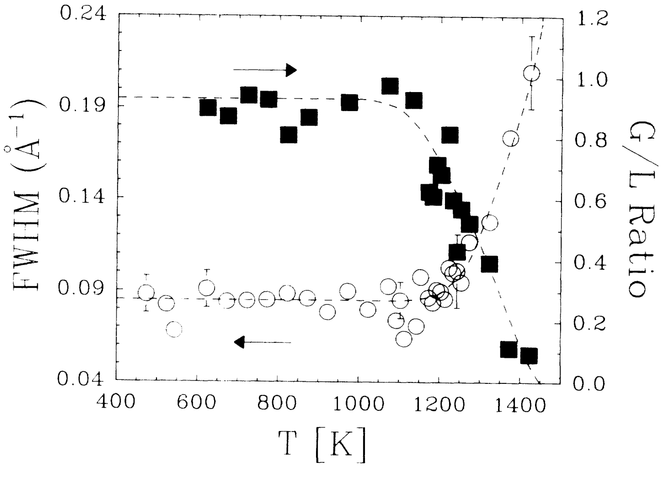

FIG. 4. The ratio of the Gaussian to Lorentzian intensity (■) and the Lorentzian FWHM (○) vs temperature for constant $Q_\perp = 2.52\text{-Å}^{-1}$ scans across the (110) peak ($E = 300$ eV, $\theta_i = 163.6°$). Dashed lines are a guide to the eye.

sion coefficient, α, is related to the anharmonicity through both the Grüneisen parameter, γ, and the isothermal compressibility, κ, by $\alpha = \gamma c_v \kappa/3$, where c_v is the constant-volume heat capacity. Because γ and κ are larger for a more anharmonic potential, the surface expansion coefficient must be larger than in the bulk. An enhanced expansion of the top layer of an fcc (110) surface near T_m has been reported by MDS.[16] We suggest that this difference builds in a large stress in the surface region above 900 K.

The surface has two mechanisms for reducing this stress. First, the surface atoms may become incommensurate with the bulk. This type of deformation has been seen in previous studies on Au(100).[18] An incommensurate layer is not seen on this system. Unlike most metal surfaces, the vertical relaxation of the first-layer atoms on Ni(110) is large, indicating a strengthening of the back bonds normal to the surface.[19] For Ni, this may effectively pin the top layer to the bulk. The second method for reducing the stress is to decrease the atomic density of the top layer. This can be accomplished by either increasing the vacancy concentration or by increasing the step density. Simulations using Lennard-Jones or effective-medium potentials show that the energy for vacancy formation is lower on (110) surfaces.[14,20] At high enough vacancy concentrations defect clustering becomes important, forming stepped surface regions, and the surface roughens. Whether or not the height correlation function diverges logarithmically[17] above 1350 K has not yet been determined.

The experiments outlined above show that, contrary to previous studies, Ni(110) does indeed roughen at a temperature of $\sim 0.75 T_m$. The roughening of the surface is preceded by two stages. First, a large increase in $\langle u^2 \rangle$ at 0.5 T_m suggests an anharmonicity developing in the surface Ni-Ni potential. Qualitatively the vibrational amplitudes are observed to be twice as big in the plane of the surface as perpendicular to it. The difference in the anharmonicity of the surface and the bulk suggests that a stress is introduced in the surface layer. Experiments are under way to directly measure the expected vertical expansion of the top layer. Finally, the surface begins to form vacancies that are about 10% of the surface density between 1200 and 1300 K. Above 1350 K the probability of making a step increases dramatically and the surface roughens.

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