Anomalous thermal behavior of the Fe(100) surface observed by grazing ion-surface scattering

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We show that scattering of 25-keV He^+ ions under the condition of planar surface channeling offers a sensitive technique to study the thermal behavior of metal surfaces. The angular distributions of scattered projectiles directly depend on thermal displacements of surface layer atoms and reveal characteristic features caused by scattering at surface steps. Based on computer simulations we deduce an anomalous increase of the mean-square displacement normal to the surface for temperatures above about 750 K. An increase in the density of surface steps can be excluded. [S0163-1829(97)00147-1]

The thermal behavior of crystal surfaces has been found to comprise phenomena of fundamental interest such as anharmonic vibrations of lattice atoms, structural roughening, or premelting.[1,2] The loosely packed (110) surfaces of fcc crystals have served as prototype systems to study such processes. Various surface sensitive techniques such as diffraction of thermal atoms or x rays have been used to study the anomalous thermal behavior of Cu(110) (Refs. 3–7). Conclusions drawn from experiments were contradictory due to difficulties in discriminating between possible processes contributing to thermal disordering. By now there seems to be a consensus on an anomalous increase of the thermal elongations of the Cu surface atoms for temperatures $T \geqslant 550$ K. In contrast to Cu(110), fewer studies have been reported on anharmonic effects for other crystal surfaces, such as Pb(110),[8] Ni(100),[9] Ni(110),[10] Ag(110),[11] Ag(111),[12] and Cu(100).[13] These are fcc crystals and the question arises whether anharmonic effects are a more general phenomenon occurring at surfaces of, e.g., bcc crystals as well.

Scattering of fast ions or atoms offers a natural and direct tool to study surface lattice vibrations. The advantage of making use of ion beams are (1) phonon frequencies are orders of magnitude smaller than ion-atom interaction frequencies, i.e., the ions experience instantaneous thermal displacements of atoms from their lattice positions; (2) the scattering process can be described within the frame of classical mechanics; (3) the penetration depth can be minimized to the surface layer by using appropriate scattering geometries. In the past, information on surface-lattice vibrations has thus been obtained with ions or atoms incident at large angles with respect to the surface plane by making use of the concept of shadow-cones.[6,14–16]

In the present paper we propose an alternative method to study the thermal behavior of surfaces. A beam of 25-keV He^+ ions is incident under a grazing angle upon the (100) surface of bcc Fe. The projectiles are steered by the repulsive planar surface potential and reflected specularly (planar surface channeling). As will be shown, angular distributions of reflected projectiles are sensitive on thermal displacements of atoms in the surface layer. Furthermore, quantitative and independent information on the density of surface steps is obtained. The latter aspect is an important advantage, since thermally generated defects at the surface and enhanced thermal vibrations are physically related but difficult to separate in experiments. Moreover, our technique solely probes the topmost surface layer. This avoids difficulties in extracting information on anharmonicities, which are always related to changes in interplanar distances due to thermal expansion.[1]

The experiments are performed in a UHV chamber at a pressure in the lower 10^{-9} Pa range. A beam of 25-keV He^+ ions is collimated by sets of horizontal and vertical slits (width 0.2 mm) to a maximum angular divergence of $\pm 0.02°$. The beam is directed on the Fe(100) surface at a grazing angle $\Phi_{in} \approx 1.5-2.0°$ along a high-index surface-lattice direction (random incidence) (see Fig. 1). Reflected projectiles are recorded by a channeltron detector as a function of the polar scattering angle Φ_s. The detector is mounted on a precision manipulator which is moved in the plane of scattering by means of a stepmotor. A 0.5-mm diaphragm in front of the channeltron defines an angular acceptance of $\pm 0.02°$. The current density of the incident beam is typically 50 nA/mm^2, resulting in channeltron count rates of about 8×10^4 s^{-1} in the maximum of the angular distribution.

The preoriented (100) Fe single-crystal disk (diameter 9 mm) was carefully aligned and polished (residual miscut angle $<15'$). *In situ* preparation of the (100) surface was performed by frequent cycles of grazing Ar^+ sputtering and subsequent annealing at 920 K. It took about two months to finally obtain a clean and well-ordered surface as checked by Auger electron spectroscopy and low-energy electron diffraction. Suitable setting of the preparation parameters (grazing incidence angle, time of sputtering, and annealing) enables one to choose the density of steps at the surface.

The Fe crystal exactly fits into a bore of a small iron block, which can be resistively heated. This ensures a homogeneous and constant surface temperature. The temperature is measured by a thermocouple with low heat capacity, which is attached to the front of the iron block close to the crystal surface. The temperature can be held constant to ± 1 K; the absolute accuracy is estimated to be better than ± 20 K.

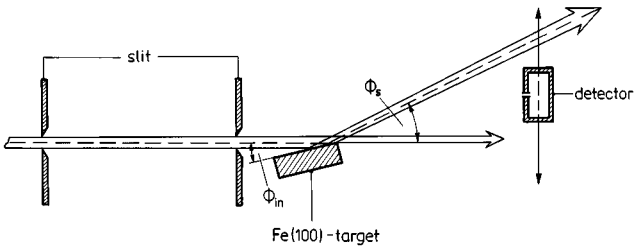

FIG. 1. Sketch of the experimental setup.

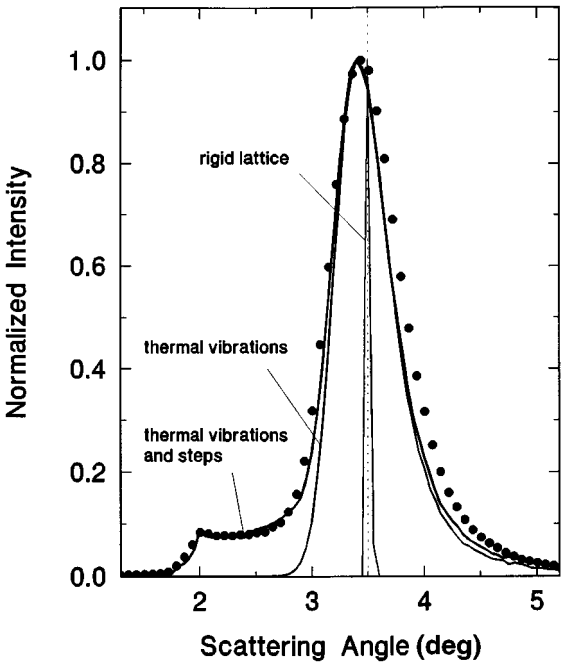

FIG. 2. Normalized measured (circles) and simulated (lines) polar angular distributions for 25-keV He^+ projectiles scattered from an Fe(100) surface. In the experiment $\Phi_{in}=1.75°$ and $T=600$ K. The simulations were performed for $\Phi_{in}=1.75°$ and (1) a perfect, rigid surface lattice, (2) a perfect surface but with thermally elongated atoms ($T=600$ K, $T_\perp^S=227$ K), and (3) a surface where, in addition to thermal elongations, geometrically distributed ascending and descending steps with a mean distance of 500 Å and monatomic step heights are incorporated. In each case 10^6 projectiles were simulated. The dashed vertical line indicates specular reflection ($\Phi_s=2\Phi_{in}$).

Figure 2 shows a typical angular distribution (circles) for $\Phi_{in}=1.75°$ and $T=600$ K. The distribution consists of a narrow, nearly Gaussian peak with its maximum slightly below the angle for specular reflection ($\Phi_s=2\Phi_{in}$) and a steplike structure at smaller scattering angles. In order to describe the observed angular distributions we performed Monte Carlo computer simulations using the sequential binary collision model.[17,18] The pairwise interactions are described by the Thomas-Fermi-Molière potential with a screening length as proposed by O'Connor and Biersack.[19] We first simulated a perfect and rigid semi-infinite Fe(100) crystal, i.e., neither thermal elongations nor defects are included. The angular distribution of scattered projectiles shows an almost δ-shaped peak at $\Phi_s=2\Phi_{in}$, i.e., all projectiles are specularly reflected as expected from the concept of planar surface channeling.

We then took into account thermal vibrations using the harmonic model, i.e., by a Gaussian probability density function of the lattice atoms.[20] The mean square displacements $\langle u_\perp^2\rangle$ and $\langle u_\parallel^2\rangle$ perpendicular and parallel to the surface plane, respectively, are calculated from surface Debye temperatures $T_\perp^S$ and $T_\parallel^S$ using the relation

$$\langle u_{\perp,\parallel}^2\rangle = 3\hbar^2 T/Mk(T_{\perp,\parallel}^S)^2, \tag{1}$$

where M is the mass of the Fe lattice atom and the other symbols have their usual meanings. Whereas the influence of parallel displacements turned out to be negligible, displacements perpendicular to the surface strongly broaden the angular distribution (see Fig. 2). A closer inspection shows that this broadening is asymmetric; the maximum slightly shifts to smaller angles (subspecular reflection) and a tail evolves at large scattering angles. Both features are found in the experimental data.

However, the simulation does not describe a steplike structure observed at small scattering angles. We thus incorporate surface steps by simulating a random sequence of ascending and descending steps with monatomic step height and geometrically distributed step distances. This almost perfectly reproduces the observed angular distribution (see Fig. 2). The steplike structure sets in at the edge of the shadow cast by the target ($\Phi_s=\Phi_{in}$), and the height of its plateau is given by the mean distance between steps. It is caused by scattering of the projectiles at *de*scending steps due to the sudden weakening of the repulsive planar potential when the projectile crosses a step edge. In contrast, projectiles hitting an *a*scending step are scattered by large angles and do not contribute to the measured angular distribution. We note that under our conditions surface steps hardly contribute to the width of the main peak.

For the sake of transparency, our simulation completely neglects electronic processes. Such processes are supposed to additionally broaden the angular distribution (e.g., multiple scattering by electrons, fluctuations in charge states of the projectiles,[21] image charge effects[22]). In fact, they are found to dominate for $\Phi_{in}\lesssim 1°$, where the projectiles do not approach the surface atoms closely enough in order to feel their thermal displacements. In the present case this contribution is small (see Fig. 2) and can be considered by an off-line convolution. Moreover, in the spirit of the Born-Oppenheimer approximation, it should not depend on the temperature.

In conclusion we found that the angular distributions mainly result from normal surface lattice vibrations and surface steps. These two effects do not interfere and give rise to the broadening of the peak and the steplike structure, respectively. Thermal roughening and anharmonic effects can thus be discriminated unambiguously.

Measured angular distributions for a constant $\Phi_{in}=1.85°$ are shown in Fig. 3 (circles) as a function of the surface temperature. As anticipated the distributions grow broader with increasing temperature. At $T=473$ K the observed distribution is well reproduced by the simulation (solid line) for a stepped surface (mean step distance 400 Å) and a surface Debye temperature $T_\perp^S=227$ K.[23] The small residual deviation in width is ascribed to electronic processes and amounts to the same value as in Fig. 2. Yet the deviation gets larger with increasing temperature; above 800 K, the observed distributions are significantly broader than the simulated curves. Since all simulations are performed with the same surface Debye temperature, this means that the thermal displacements at the highest temperatures are larger than expected from the harmonic approximation.

In contrast to the width of the distribution, the observed height of the steplike structure is well reproduced by the simulation for all temperatures. Hence the density of surface steps does not change. In particular, a proliferation of steps or roughening transition can be excluded.

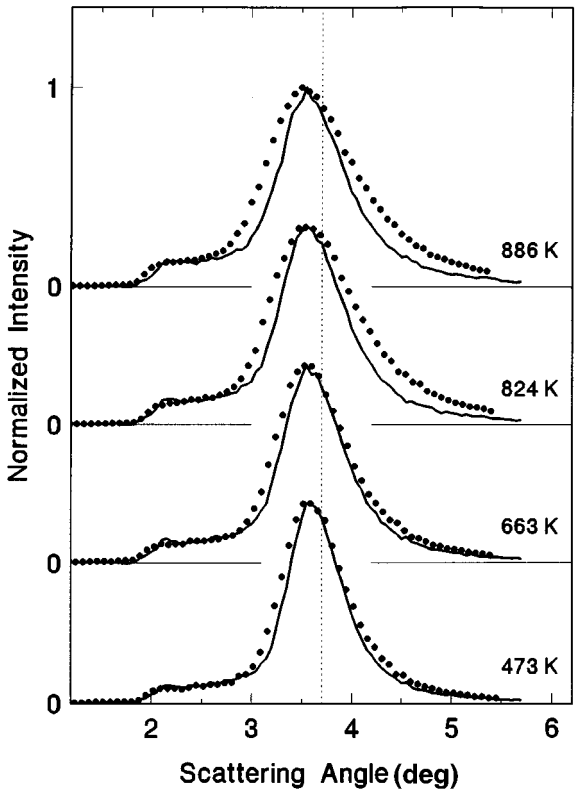

FIG. 3. Normalized measured (circles) and simulated (lines) polar angular distributions at different temperatures. $\Phi_{in}=1.85°$. The simulations were performed for a stepped surface (mean step distance 400 Å) and a surface Debye temperature $T_{\perp}^{S}=227$ K (solid lines). The dashed vertical line indicates specular reflection.

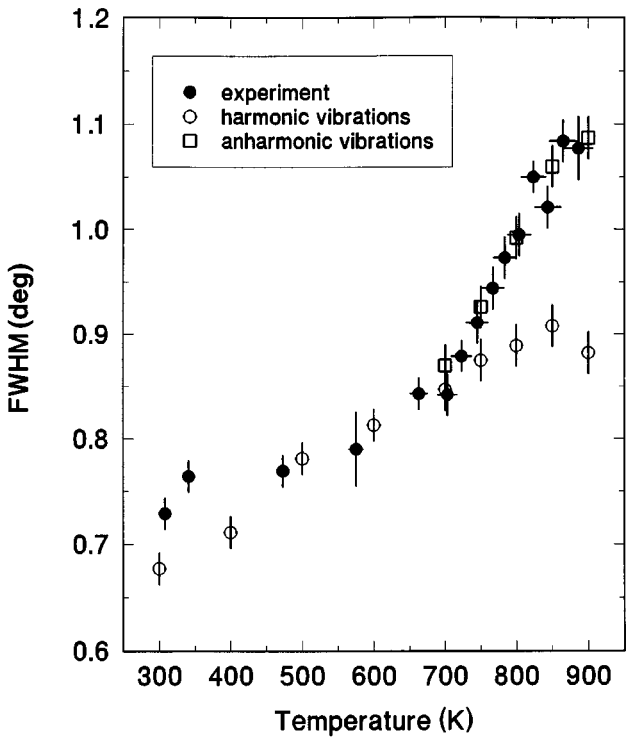

FIG. 4. FWHM of measured (solid circles) and simulated (open symbols) angular distributions. $\Phi_{in}=1.85°$, mean distance between surface steps 400 Å. Open circles are the results with thermal displacements from the harmonic model; open squares are best-fit data for anharmonic vibrations.

In Fig. 4 the full widths of half maximum (FWHM's) of experimental (solid circles) and simulated (open symbols) angular distributions are plotted as a function of temperature. The harmonic approximation (open circles) holds for surface temperatures up to 700 K. At larger temperatures the experimental FWHM's rise much faster than the simulated data. This deviation is interpreted by anharmonic vibrations, i.e., with increasing temperature surface atoms experience the anharmonic parts of the effective one-particle potentials. In order to quantify this anharmonicity we adopt in our simulation a quasiharmonic approach, where the actual probability density function is approximated by a Gaussian function with a mean-square displacement calculated from a Debye temperature that is allowed to be temperature dependent. A fit to the experimental data yields $T_{\perp}^{S}=215$ K at 700 K, 200 K at 750 K, 180 K at 800 K, 170 K at 850 K, and 160 K at 900 K (Fig. 4, open squares). The corresponding mean square displacements $\langle u_{\perp}^{2}\rangle$ are calculated from Eq. (1) and compared in Fig. 5 (solid circles) with a linear increase as expected from the harmonic model (solid line).

Molecular-dynamics computer simulations on Cu(110) revealed a close relationship between an enhanced anharmonicity and defects at the surface (steps, adatoms, vacancies).[24] We therefore repeated the measurements for surfaces with largely different step densities as inferred from the plateau of the steplike structure in the angular distribution. No dependence of the anharmonicity on the mean step distance could be observed, i.e., there is no indication of a first-order or second-order (through adatoms originating from step edges) influence. As to thermally generated adatom-vacancy pairs, our data are less conclusive. Though the effect of an adatom on the projectiles' trajectories is similar to an ascending step and leads to large-angle scattering, vacancies or defect cluster configurations may contrib-

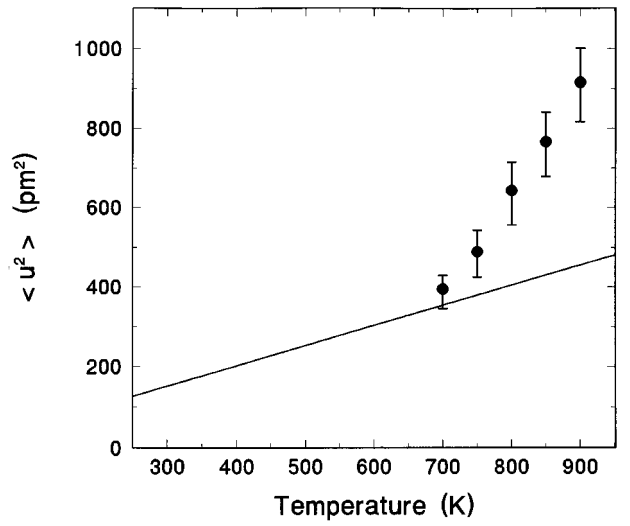

FIG. 5. Mean-square displacement normal to the surface of an Fe(100) surface atom as a function of temperature as obtained by a fit to the experimental data. The solid line represents the linear dependence as expected from the harmonic model.

ute to a broadening of the angular distributions. We thus cannot exclude that adatom-vacancy generation driven by enhanced vibrations occur. In contrast, adatom proliferation of segregated impurities[25] can be excluded, because experimental results were completely reproducible even after prolonged heating of the target.

In summary, we showed that scattering of fast ions in the regime of planar surface channeling offers a direct and sensitive technique to study the thermal behavior of the topmost layer of crystal surfaces. For suitably chosen incidence angles, the angular distribution of reflected projectiles depends in a characteristic manner on thermal vibrations normal to the surface and reveals features caused by scattering at surface step edges. The angular distributions can be described by simple Monte Carlo simulations within the frame of classical mechanics. This enables one to deduce thermal displacements of topmost surface layer atoms and the density of steps.

By scattering of 25-keV He^+ ions at the (100) surface of bcc Fe, we find evidence for anharmonic vibrations of the surface lattice atoms for temperatures $T > 750$ K. An increase in the step density can be ruled out in the temperature range studied. Our results indicate that anharmonic effects are a general phenomenon not restricted to surfaces of a few fcc crystals. The anharmonicity develops at roughly half of the melting temperature of Fe, in accordance with the apparent universality found for the fcc surfaces studied.[1]

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