# Investigation of surface defects on Ni(110) with a low-energy positron beam

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The trapping of positrons at surface defects that develop during the epitaxial growth of a Ni film on a Ni(110) substrate is established. Trapping is detected by the resultant decrease in positronium that is formed by electron capture at the surface after the incident 900-eV positrons thermalize in the target. Ion-bombardment-induced defects are also investigated. It is found that ledges are the dominant trapping site on both surfaces. The average ledge spacing on the ion-bombarded surface, after annealing at a specified temperature, is determined by analyzing the broadening of low-energy electron diffraction (LEED) spot profiles. This spacing is then used to calibrate the positronium formation results on each of the annealed surfaces. These results, when applied to the Ni-on-Ni(110) film (where LEED spot broadening is too small to be resolved), yields a measurement of the island nucleation density.

## I. INTRODUCTION

Surface defects play an important role in determining the physical and chemical properties of surfaces.[1] Low concentrations of surface defects measurably influence a metal's work function and can dominate the chemical activity of the surface for particular reactions.[2,3] A variety of techniques, including transmission electron microscopy (TEM), low-energy electron diffraction (LEED), work-function measurements, x-ray and uv photoemission, and low-energy ion and atom scattering have contributed to the present understanding of the geometric and electronic structure of surface defects.[4–6] The information concerning defects is often extracted from a signal dominated by the translationally ordered portions of the surface and thus the sensitivity of such techniques is severely limited when the defect density is low. The ideal probe for low-density defects would be insensitive to the ordered areas of the surface and preferentially interact with defect sites.

It is well known that positrons thermally diffusing within a metal preferentially interact with *bulk* defects, typically vacancies, which trap the positrons.[7] The vacancy's large cross section for trapping, coupled with the long bulk diffusion length of positrons ($\sim 10^3$ Å), results in a large fraction of them annihilating in these traps when the trap density approaches $10^{18}$ cm$^{-3}$. Low-energy (10 eV–10 keV) positron beams with penetration depths comparable to the thermal diffusion length have recently been used to study near surface and interface defects, and adsorbates.[8–11] Typically, the trapping of positrons at defects is detected by the attendant reduction in the reemitted positron yield (if the surface has a negative positron work function) or the decrease in positronium formation that occurs at the surface. These experiments clearly demonstrate that positrons are trapped at near-surface defects, predominantly vacancies, for which the detection by other techniques is difficult. However, the sensitivity of positrons to purely surface defects such as isolated adatoms, monovacancies, and steps and kinks of ledges was left unresolved.

In this paper we report the results of an initial study to probe the sensitivity of positronium formation to purely surface defects. Two-dimensional defects are added to the surface by the thermal vapor deposition of submonolayer amounts of Ni on a clean well-annealed Ni(110) surface. The anticipated density of these surface defects depends strongly on coverage: at very low coverage isolated adatoms dominate; near monolayer coverage the defects are more likely to be associated with island ledges or surface vacancies. Using established models of epitaxial growth the first determination of the predominant surface trapping sites for positrons is made. The surface density of island nucleation sites on Ni(110) at 350 K is estimated.

In a similar experiment, designed to correlate our results with terrace length determinations by LEED, near-surface defects are created on Ni(110) by Ar-ion bombardment and annealing at various temperatures. Bombardment erodes the surface producing pits which, on a microscopic scale, consists of steps and terraces of various lengths that expand on annealing. The characteristic terrace length is directly measured from a spot profile analysis of a diffracted LEED beam and then correlated with the corresponding formation fraction of positronium measured on that surface. Our results are consistent with a model in which defect trapping occurs at the step sites on the perimeter of terraces, the density of such defects decreases as the terrace size increases. LEED spot profile analysis could not be used for the Ni film experiment because the profile broadening is too small to be resolved by our commercial LEED apparatus. In the next section we present experimental details and results along with our qualitative conclusions. In Sec. III the results are quantitatively analyzed using a positron diffusion model in which defect trapping at the surface is included. In Sec.

 

IV we discuss some of the unresolved questions that future refinements in this positron technique should address.

## II. EXPERIMENTAL PROCEDURE AND RESULTS

All experiments were performed in an ultrahigh-vacuum surface-analysis chamber interfaced to a low-energy positron beam. The analysis chamber is equipped with facilities for LEED, Auger spectroscopy, ion sputtering, and residual gas analysis. The base pressure of the system is $10^{-10}$ Torr with the pressure rising to $10^{-9}$ Torr during Ni evaporations. The Ni sample was cleaned by repeated cycles of ion bombardment (2-keV Ar ions incident at 75°) and thermal annealing. Small residual amounts of carbon remaining after this procedure were removed by flash desorption of adsorbed oxygen at 1000 K.

The positron beam and positronium detection technique will be only briefly discussed since they have been described in Ref. 12. Low-energy positrons from a $^{22}$Na source and W-vane moderator[13] are electrostatically accelerated to 900 eV and focused onto the Ni(110) crystal. At this energy a large fraction of the positrons thermalize within a diffusion length of the surface. Positrons reemitted from the surface are returned by a positively biased retarding grid. Positronium (Ps) formed by electron capture at the surface is efficiently distinguished from all other positron decay processes by the long ($\sim$140 nsec) lifetime of the triplet spin state. Start and stop signals for a time-to-amplitude converter-multichannel analyzer timing system are derived from the detection of secondary electrons ejected by the incident positrons and from the subsequent detection of annihilation $\gamma$ rays. The total positronium formation fraction $f$ is determined from the ratio of long-lived events (between 30 and 405 nsec) and the total number of events in the background-corrected lifetime spectrum. Neglecting the systematic uncertainty of about 5% in converting the raw ratio of counts into $f$ (which is the same for all runs), $f$ can be measured to a statistical accuracy of about 0.5% in a 5-min run.

In the first experiment the Ps formation fraction, $f$, is measured after Ni is evaporated onto the (110) surface of a Ni sample that has previously been annealed to 1350 K. Such a deposition clearly does not roughen the substrate surface or create subsurface defects. Estimates of the Ni coverage were made with a polycrystalline Ta foil attached to the sample holder by monitoring the attenuation of the 179-eV Ta $LVV$ Auger transition during the evaporation. This attenuation permits the Ni-on-Ta coverage to be determined[14] from the mean free path of 179-eV electrons in Ni. The Ni-on-Ni(110) coverage can then be estimated with an overall systematic uncertainty of order 50%. In addition, the Auger spectra showed trace contamination of CO on the surface after several depositions.

The measured values of $f$, shown in Fig. 1, indicate a strong coverage dependence when the substrate temperature is 350 K. This dependence of $f$, together with well-developed models of epitaxial growth,[4,5] can yield qualitative insight into the interaction of positrons with surface defects. At very low coverages ($\Theta$=0.025) Monte Carlo simulations[15] on Ni(100) at 350 K show that only a few percent of the deposited Ni is present as isolated adatoms.

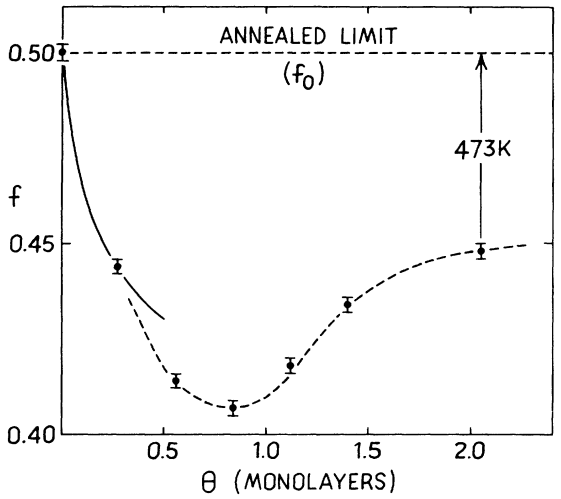


FIG. 1. The positronium formation fraction $f$ versus coverage of evaporated Ni on a Ni(110) substrate held at 350 K. The dashed line is intended to guide the eye. The solid line through the first two points is the result of a simple diffusion-model calculation in which no layer stacking is assumed (see Sec. III for discussion).

Thus we expect that virtually all the adatoms at $\Theta$=0.28 (our lowest coverage) should form two-dimensional (2D) islands with their perimeters bounded by monolayer high steps. The marked attenuation of $f$ at this and higher $\Theta$ indicates that positron trapping can occur at these steps surrounding the islands. At $\Theta$ near 0.8, where $f$ reaches a minimum, adatoms are removing and creating trap sites with equal probability. This is consistent with the merging of islands and a resultant decrease in perimeter step sites as the first monolayer tends to be completed. At still higher coverages $f$ increases though remains lower than $f_0$, the annealed limit. We attribute the failure of $f$ to completely return to $f_0$ at $\Theta$=1.0 to the stacking of a second or higher layers of Ni islands on the top of the still incomplete first layer (and, in part, to the trace CO contamination which, in separate measurements, is observed to reduce $f$). Some island stacking is expected at this low temperature and similar nonperiodicities or damping of oscillatory behavior have been observed with LEED and reflection high-energy electron diffraction (RHEED) during epitaxial growth of semiconductor surfaces.[16] Heating the sample to only 473 K (well below the bulk annealing temperature of about 900 K) after the final deposition returns $f$ to $f_0$, indicating that only surface diffusion processes are needed to reform the surface.[17] This result also strengthens our conclusion that step sites are the predominant trapping sites since low-energy ion scattering from steps on Ni(110) is also observed to disappear at temperatures above 400 K.[6]

While the above qualitative considerations permit step sites to be identified as the surface defect which traps positrons, a detailed picture of this interaction is more difficult to obtain. The difficulty of extracting quantitative information, such as trapping cross sections, results from the lack of independent measurements of the density of

step sites during the epitaxial growth. The step density resulting from the distribution of island sizes on the surface can be determined from spot profiles of a LEED beam.[18] The presence of islands and other defects, which disrupt the long-range order, increases the angular width of the diffracted beam in a characteristic manner. Island size can be estimated by analogy to a 2D diffraction grating. For an $N \times N$ array of atoms separated by a nearest-neighbor distance of $a$, the half-width of the beam is

$$\Delta = \lambda/(2Na\cos\Phi) , \tag{1}$$

where $\lambda$ is the electron wavelength and $\Phi$ is the exit angle of the electron.[19] Spot profiles of the (10) beam were measured along the [111] direction using a spot photometer with a 0.033° aperture. The instrumental limit of the LEED arrangement is approximately $Na = 180$ Å. Observation of the (10) beam after the deposition of one monolayer showed no significant change in the spot profile. Apparently the island sizes are too large or the island densities too low to measure with this apparatus.

To generate a readily measurable concentration of surface defects the Ni(110) surface was bombarded with 2-keV Ar ions at room temperature until the LEED spot profiles were visibly broadened. Bombardment was continued to saturation (no further broadening). The morphology of the Ni surface damaged by ion bombardment has been carefully studied.[20] From the observed broadening and splitting of diffracted beams these studies conclude that saturation ion doses produce surface pits consisting of terraces separated by single atomic steps $\sim 50$ Å apart. Annealing increases the terrace widths, eventually removing the surface pits. Equating the atoms along the ledges of these sputter-induced terraces with the atoms on the perimeter of the islands present during epitaxial growth provides a link between the two surfaces. However, on the sputtered and annealed surface a measurement of the terrace width, Na in Eq. (1), at each annealing temperature can be determined and the corresponding value of $f$ measured. The instrumental contribution to the spot profile was removed by assuming a Gaussian resolution function. The sensitivity of $f$ to the terrace width is shown in Fig. 2. For small, 80-Å terraces positrons frequently encounter the defects associated with the ledges and are trapped, reducing $f$ by a factor of 2. It is not until the terraces are larger than 200 Å that $f$ increases significantly. This suggests that positrons either sample a large number of surface sites or that they can be trapped over a very long range. This point, as well as the role that subsurface vacancies on the sputtered surface play in trapping positrons, will be considered in the next section where we attempt a more quantitative analysis.

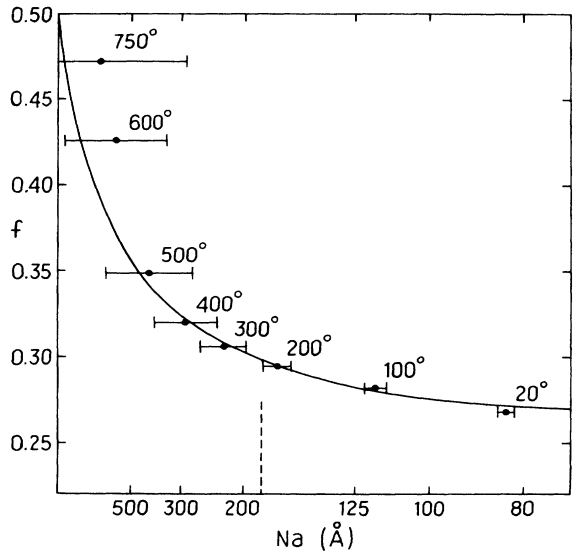


FIG. 2. Values of $f$ measured on the sputtered and annealed Ni(110) surface are plotted versus the average terrace width, Na, as determined from the LEED beam spot profiles. An inverse scale is used, the annealing temperature (in °C) for each run is shown, and the LEED instrumental resolution of 180 Å is denoted by the dashed marks. The error bars in Na are due to uncertainties associated with deconvolving the instrumental resolution. The solid line is a calculation and fit of $f$ to these data using the diffusion model discussed in Sec. III.

## III. ANALYSIS AND DISCUSSION

To relate the density of surface traps on the sputtered and annealed sample to $f$, the Ps formation fraction, we present a simple model based on a classical description of the positron's motion. We begin with the diffusion model of Nieminen and Oliva.[21] For positrons implanted a depth $z$ below the surface with stopping profile $S(z)$,

$$f = \frac{\nu_{Ps}}{\nu_T + \sqrt{\lambda D}} L[S(z)] , \tag{2}$$

where $\lambda$ and $D$ are the bulk annihilation decay rate and the bulk diffusion constant, respectively, and $L[S(z)]$ is the Laplace transform of $S(z)$ (see Ref. 21). The parameters $\nu_{Ps}$ and $\nu_T$ represent the rate at which Ps formation alone ($\nu_{Ps}$) or all surface loss processes ($\nu_T$, including bare positron reemission, surface trapping, and Ps formation) remove positrons from diffusing in the bulk. These surface rates should depend on an effective surface density times a cross section and on the positron velocity $v$. We remove this explicit dependence on $v$ by defining probabilities $P_{Ps}$ and $P_T$ such that

$$\nu_{Ps} = P_{Ps} v$$

and (3)

$$\nu_T = P_T v .$$

Thus $P_{Ps}$ and $P_T$ are the respective loss probabilities per surface encounter (and they may still depend on velocity through any temperature dependence of the respective cross sections—all measurements were, however, carried out at a constant temperature of 350 K).

On a surface with additional trapping defects we take $P_d$ to be the positron defect trapping probability per surface encounter and modify $P_{Ps}$ and $P_T$ to be

$$\begin{aligned} P_{Ps} &= P_{Ps,0}(1-P_d) + \epsilon P_d , \\ P_T &= P_{T,0}(1-P_d) + P_d , \end{aligned} \tag{4}$$

where $P_{Ps,0}$ and $P_{T,0}$ correspond to their respective values on an undamaged surface. Thus $P_d$ is, in effect, the damaged fraction of the surface as sampled by the positron (see discussion below). The term $\epsilon P_d$, the probability that a trapped positron can still form Ps, phenomenologically accounts for the fact that $f$ does not go to 0 as $P_d$ approaches unity, as seen in Fig. 2. Inserting these results into Eq. (2) and neglecting the small bulk diffusion term, we find

$$f=\frac{P_{Ps,0}(1-P_d+\epsilon P_d/P_{Ps,0})}{P_{T,0}(1-P_d+P_d/P_{T,0})}L[S(z)]\ . \tag{5}$$

Normalizing $f$ to $f_0$, where $P_d=0$, removes $S(z)$ from the equation. Therefore $R=f/f_0$ is given by

$$R=\frac{1-P_d+0.5P_d/P_{T,0}}{1-P_d+P_d/P_{T,0}}\ , \tag{6}$$

where $\epsilon$ has been determined by inspecting $R$ in the limit of $P_d=1$.

The probability $P_d$ will depend on the density and shape of the islands or terraces on a surface, as well as a trapping cross section (at 350 K). For the sputtered surface we assume the surface consists of square terraces of characteristic length $l$ as shown in Fig. 3. We identify an effective range $\xi$ near a ledge within which a positron is trapped during a surface encounter (i.e., the trapping cross section of a ledge is $2\xi l$). By geometry, the "damaged" surface fraction is $P_d=1-(1-2\xi/l)^2$. With this expression for $P_d$ in Eq. (6), the data in Fig. 2, after normalization to $f_0=0.50$, are fit quite well when $\xi/P_{T,0}\approx 100-150$ Å as shown by the solid line. This result is surprising because it is so large. The length $\xi$, related to the positron's de Broglie wavelength, is presumably restricted in a metal by the electron screening cloud to several screening lengths. Then $\xi\lesssim 5$ Å and it follows that $P_{T,0}<0.05$.

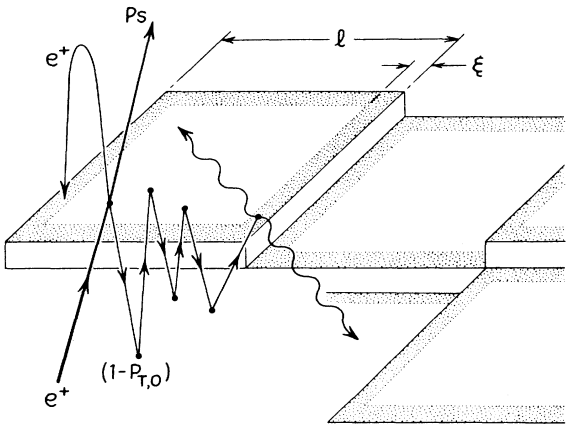


FIG. 3. A schematic representation of our surface model in which terraces (or islands) of size $l$ are surrounded by steps which trap positrons when they encounter the surface within a length $\xi$ of the ledge. Several possible fates of a positron that has diffused back to the surface are shown, including formation of Ps, direct reemission and return to the surface by the applied retarding electric field, and multiple internal reflection and eventual annihilation after trapping near a step.

This implies that a positron is internally reflected from the undamaged surface of Ni with 95% probability. If this is the case the positron reencounters the surface many times, giving it an effective range over the surface of order 100 Å. Theoretical calculations[21] of the internal reflection coefficient are generally consistent with our value. However, there is little experimental evidence[22] supporting such high internal reflectivities. We note this point since our measured value of $\xi/P_{T,0}$ may have been increased by any sputtering-induced subsurface defects[11] that, in our analysis, would effectively increase the deduced surface damaged area and thus $\xi$. Therefore we consider $\xi/P_{T,0}\approx 100$ Å to be an *upper limit* when we apply this result to the Ni-on-Ni(110) epitaxial growth experiment.

If we apply this diffusion model to the epitaxial growth of the Ni film we assume as before that trapping occurs within a distance $\xi$ of the perimeter of an isolated island. At low coverages ($\Theta<0.5$) the probability of a positron being trapped at an island ledge in a single surface encounter is

$$P_d=8\xi\sqrt{n}\,\sqrt{\Theta}\ , \tag{7}$$

where $n$ is the island density, or nucleation site density. Inserting this expression into Eq. (6) and fitting it to the first two points in Fig. 1 (as shown by the solid line) yields $\xi\sqrt{n}/P_{T,0}=0.07$. From above, the upper limit of $\xi/P_{T,0}<100$ Å then yields $n>5\times10^9$ cm$^{-2}$. Several independent determinations of $n$ during the epitaxial growth of metal films on metal substrates have been made in ultrahigh vacuum (UHV) environments with a TEM. For Pb and Pd on Ag(111), $n=2\times10^9$ cm$^{-2}$ at 300 K and $n=3\times10^{10}$ cm$^{-2}$ at 423 K, respectively.[23] A model of the nucleation process[4] that accounts for the rate of deposition and the substrate temperature predicts a range of values for $n$, $5\times10^9$ cm$^{-2}<n<10^{11}$ cm$^{-2}$, for our growth conditions. The overall agreement of our present determination of island density with both model calculations and independent measurements is an encouraging sign that a consistent view of positron defect trapping at the surface is emerging in this work. We note that by treating the island-covered epitaxial film surface in a consistent way with the sputter-annealed surface (with its measured terrace lengths) we can deduce $n$ by eliminating the parameter $\xi/P_{T,0}$, which depends on the detailed physics of the positron-surface interaction and the trapping mechanism. Thus our result depends mainly on the compatibility of the respective surface morphologies and not on a detailed (and largely unknown) knowledge of the positron-surface interaction.

## IV. CONCLUSION

We conclude that the Ps formation fraction is strongly affected by the presence of particular surface defects. On both sputtered and evaporated Ni surfaces the dominant positron trap is associated with the ledges surrounding the terraces or islands. On the sputtered Ni surface, where we can determine the average terrace size from the broadening of LEED beam profiles, we find that our technique derives some of its high sensitivity through the positron

encountering the surface many times during the diffusion process. This produces an effective trapping length $\xi/P_{T,0}$ as large as 100 Å. With this upper limit we can then set a limit on the island density for Ni film growth of $n > 5\times10^{9}$ cm$^{-2}$. As the islands merge together near $\Theta=1$ we observe an attendant increase in Ps formation as the positron-trapping ledge sites disappear in the completion of the first layer.

This technique of studying purely surface defects with positron beams seems to be a very promising probe of metal overlayer nucleation and growth. As a defect probe it complements standard LEED systems because it is most sensitive when the defect spacing exceeds 200 Å (as shown in Fig. 2), whereas LEED is typically useful below 200 Å. However, several questions must still be answered. In particular, the role of isolated adatoms and surface monovacancies is still unresolved. Very delicate, low deposition ($\Theta\approx0.01$) studies with low substrate temperature where surface diffusion is restricted are required. On the other hand, future measurements at higher substrate temperature, or with other film-substrate combinations, where surface diffusion is enhanced, may show completely periodic layer-by-layer growth without the complexities of incomplete layer stacking. Finally, the influence of defects produced for film-substrate combinations that exhibit strained layer epitaxy should be investigated.

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[1]*Adsorption on Metal Surfaces: An Integrated Approach,* edited by J. Benard (Elsevier, Amsterdam, 1983).

[2]R. Smoluchowski, Phys. Rev. **60**, 661 (1941).

[3]R. K. Sherburne and H. E. Farnsworth, J. Chem. Phys. **19**, 387 (1951).

[4]J. A. Venables, G. D. T. Spiller, and M. Hanbücken, Rep. Prog. Phys. **47**, 399 (1984).

[5]K. Besocke and H. Wagner, Phys. Rev. B **8**, 4597 (1973).

[6]L. K. Verheij, J. A. Van den Berg, and D. G. Armour, Surf. Sci. **122**, 216 (1982); W. A. Schlup and K. H. Rieder, Phys. Rev. Lett. **56**, 73 (1986).

[7]*Positrons in Solids,* edited by P. Hautojarvi (Springer-Verlag, New York, 1979).

[8]K. G. Lynn, in *Positron Solid State Physics,* edited by W. Brandt and A. Dupasquier (Plenum, New York, 1983), and references therein.

[9]W. Triftshauser and G. Kogel, Phys. Rev. Lett. **48**, 1741 (1982).

[10]P. J. Schultz, K. G. Lynn, W. E. Frieze, and A. Vehanen, Phys. Rev. B **27**, 6626 (1983).

[11]A. Vehanen *et al.* (unpublished).

[12]D. W. Gidley, A. R. Köymen, and T. W. Capehart, Phys. Rev. Lett. **49**, 1779 (1982); A. R. Köymen, Ph.D. thesis, The University of Michigan, 1984.

[13]J. Van House and P. W. Zitzewitz, Phys. Rev. A **29**, 96 (1984).

[14]Layer thickness was estimated from the method of J. P. Biberian and G. E. Rhead, J. Phys. F **3**, 675 (1973), using electron mean free paths from D. R. Penn, J. Electron Spectrosc. **9**, 29 (1976).

[15]P. Schrammen and J. Hölzl, Surf. Sci. **130**, 203 (1983).

[16]J. H. Neave, B. A. Joyce, P. J. Dobson, and N. Norton, App. Phys. A **31**, 1 (1983); K. D. Gronwald and M. Henzler, Surf. Sci. **117**, 180 (1982).

[17]H. P. Bonzel and E. E. Latta, Surf. Sci. **76**, 275 (1978).

[18]H. M. Clearfield, D. B. Welkie, T. M. Lu, and M. G. Lagally, J. Vac. Sci. Technol. **19**, 323 (1981); M. Henzler, Surf. Sci. **153**, 963 (1985).

[19]S. Anderson, *Surface Science* (International Atomic Energy Agency, Vienna, 1975), Vol. I, p. 93.

[20]L. K. Verheij, Surf. Sci. **114**, 667 (1982); L. K. Verheij, J. A. Van den Berg, and D. G. Armour, *ibid.* **122**, 216 (1982).

[21]R. M. Nieminen and J. Oliva, Phys. Rev. B **22**, 2226 (1980). The relevant equation (44) has a sign error.

[22]D. A. Fisher, Ph.D. thesis, State University of New York at Stony Brook, 1984.

[23]K. Yagi *et al.*, Surf. Sci. **174**, (1979); K. Takagangi, *ibid.* **104**, 527 (1981); K. Takagangi, Ultramicroscopy **8**, 145 (1982).