Vacancy-induced disordering in the Pb(100) surface

H.-N. Yang, K. Fang, G.-C. Wang, and T.-M. Lu

Department of Physics, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

High-resolution low-energy electron-diffraction measurements reveal that the Pb(100) surface undergoes a weak disordering at about 570 K, which is 30 K below the bulk melting temperature. The disordering is preceded by an anomalous surface expansion below 480 K and then a sudden generation of a very high density of surface vacancies at 510 K. This mechanism contrasts with that of the Pb(110) surface where a surface premelting is preceded by a surface roughening transition of the Kosterlitz-Thouless type, in which multilayer steps are involved.

I. INTRODUCTION

Recently there has been intense interest in studying the disordering phenomena that occur at solid surfaces below the bulk melting temperature. A number of very powerful surface analytical techniques have been developed that allow one to probe detailed surface disordering phenomena at the atomic level. Among the low-index planes, perhaps the most well-studied surface is Pb(110)[1-5]. Medium-energy ion-channeling results revealed that the surface starts a liquidlike disordering about 100 K below the bulk melting temperature T_m of 600.7 K.[1] Although the surface premelting temperature is somewhat lower than expected, this finding is consistent, at least qualitatively, with the common belief that bulk melting is initiated by surface premelting.

One immediate question which comes to mind is, what causes the surface premelting phenomenon? Earlier molecular-dynamics (MD) simulations, using the Lennard-Jones potential which is known to describe metals poorly, predicted surface melting very close to the bulk melting temperature[6,7] ($\sim 0.95T_m$). Later, a much lower surface melting temperature was predicted by using a more realistic effective-medium theory[8] or an empirical potential[9] in the MD simulations. More recently, even these more realistic approaches encountered severe difficulties. It was found experimentally by high-resolution low-energy electron diffraction[4] (HRLEED) that the Pb(110) surface premelting is preceded by a surface roughening transition in which a high density of surface steps is generated below the surface premelting temperature. This roughening transition is of the Kosterlitz-Thouless (KT) type[10] (infinite order) in which the surface height-height correlation function diverges.[11] Neither the effective-medium theory nor the empirical potential in the MD simulations was able to predict such a roughening phenomenon, which may be due to the finite-size effect in a MD system. Instead, they observed surface vacancy formation prior to surface premelting. However, the earlier work using the Lennard-Jones potential in the MD simulation did give some evidence of surface roughening, although the prediction of surface melting is too close to the bulk melting temperature.[7]

Other theories such as lattice dynamics calculations[12] have also been proposed to describe surface premelting. These theories did not include the possibility of surface steps.

Compared to the (110) surface, very little experimental work has been performed on the (100) surface. In general, the more close-packed (100) and (111) surfaces are believed to be more stable than the (110) surface. The recent study using medium-energy ion-channeling technique shows[13] that the Pb(100) surface undergoes a continuously increased disordering as $T > 520$ K but, unlike the Pb(110) surface, it exhibits no divergent growth of the disordered thickness as the temperature approaches T_m. This peculiar thermal behavior implies the existence of a weak liquidlike disordering that does not undergo the conventional surface melting in which the quasiliquid layer diverges as $\ln[T_m/(T_m - T)]$ or $(T_m - T)^{-r}$. Liquidlike disorder has also been observed both in Au(100) (Ref. 14) and Ni(100) (Ref. 15) surfaces. The mechanism that leads to this disordering is still not clear at the present time. In this paper, we report the experimental HRLEED studies on the Pb(100) surface. Similar to Ni(100),[15] a large vertical expansion occurs in the Pb(100) surface between 300 and 470 K. More interestingly, instead of a KT roughening transition, we have observed a sudden generation of a very high density of surface vacancies at about 510 K. A weak liquidlike disordering is suggested to occur at temperatures above $0.95T_m$. The existence of the vacancy phase suggests that a distinctly different mechanism may be involved in the liquidlike disordering of the Pb(100) surface compared to that of the Pb(110) surface.

II. EXPERIMENT

The details of the experimental high-resolution low-energy electron diffractometer have been described previously.[16] The experiment was performed with a base pressure in the middle range of 10^{-11} Torr. The Pb(100) sample was spark cut from a Pb ingot in the form of a disk 6 mm in diameter and 3 mm thick. The sample was heated by thermal radiation generated from a hot Ta filament which is one loop of coiled wire circled about the cir-

cumference of the sample and having a radius of about 6 mm. This design improves the homogeneous temperature distribution of the surface and prevents the sample from overheating when the temperature is close to T_m. The surface was sputtered clean at room temperature using an argon-ion beam. Without further annealing, a sharp 1×1 LEED pattern with a square unit mesh was observed.

Room-temperature measurements of the (00) beam angular profile showed no broadening effect at the out-of-phase diffraction conditions (referring to a single atomic step height). This result indicates that the surface is free of steps within the instrumental resolution.[17] The terrace on the surface is at least 700 Å wide.

Both the angular profile of the (00) beam intensity and the background intensity were measured as functions of temperature and the incident electron beam energy. The temperature ranges from room temperature to 595 K. The background intensity was obtained at 0.18 Å^{-1}, which is about 10% of the first Brillouin zone.

III. RESULTS

A. LEED $I(E)$ curves (I-V profiles)

Figure 1 shows the measured I-V curves (normalized) for the (00) beam at various temperatures. Below 470 K, the I-V curves show no significant shape changes but the

peaks exhibit a continuous shift to low energy. This shift is attributed to the surface vertical expansion.[15] Between 300 and 470 K, the two peak positions in the I-V curves have shifted from 25 ± 0.5 and 54.0 ± 1.0 eV towards 23.5 ± 0.5 and 50.0 ± 1.0 eV, respectively. Using a simple kinematic model,[15] we estimate that the surface expansion is about 3.4% in this temperature region. The corresponding bulk thermal expansion is only about 0.48%. Therefore, from 300 to 470 K, the Pb(100) surface undergoes an anomalous surface expansion, which is at least seven times as large as that in the bulk. A similar large expansion has been observed in the Ni(100) surface,[15] which is then followed by a lateral disordering in that surface at a higher temperature.

As the temperature is raised above 470 K, the shape of the I-V curve starts to change gradually. The more significant change is observed at 550 K, as shown in Fig. 1(d). The shape of the I-V curves at $T \geq 570$ K becomes quite different from that at the lower temperatures. Despite the complexity of the multiple scattering effect, the dramatic transformation of the I-V curve still implies that a certain structural change has occurred in the Pb(100) surface.

B. Temperature-dependent peak intensity

Figure 2 shows the peak intensity as a function of temperature at two in-phase ($E=25$ and 55 eV) and two out-of-phase ($E=39$ and 73 eV) conditions. Since the I-V profiles show significant shifts at elevated temperatures, we need to correct the intensity at the fixed energy caused by the shifting of the peaks in the I-V curves, which are shown in Fig. 2 as the dashed and solid lines, corresponding to $E=25$ and 55 eV, respectively. The correction for the intensities at $E=39$ and 73 eV is negligible because the shift shows little effect on the peak intensities at the out-of-phase conditions ($<10\%$), as shown at the posi-
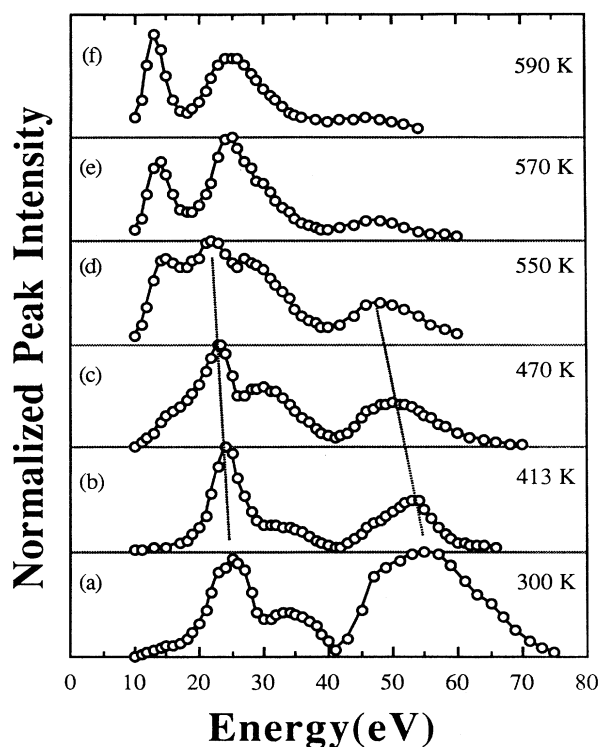

FIG. 1. The I-V curves of the specular beam are plotted at various temperatures. The dashed lines indicate the peak shifts as the temperature is increased. The incident angle of the electron beam is 3.75°.
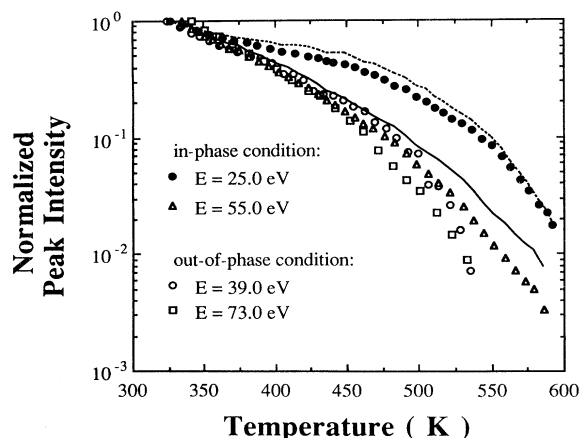

FIG. 2. The peak intensity is plotted as a function of temperature at the in-phase and the out-of-phase conditions. All the intensities are normalized to 1 at $T=330$ K. Also shown as the dashed and solid lines are the intensities corrected for the shifting of the peaks in the I-V curves at the fixed energies $E=25$ and 55 eV, respectively.

tion $E=39$ eV of the I-V curves in Fig. 1. All the measured intensities show certain degree of decay other than the usual Debye-Waller factor due to the lattice vibrations.

For both the out-of-phase and in-phase diffraction conditions, the angular profiles showed no sign of broadening or change of line shape at all temperatures within the temperature range under consideration. The results indicate that up to $T_m - 5$ K the surface is stable against step formation,[18] except possible vacancies.[19] (Although vacancies are a form of steps, they do not give a broadening of the profile but can give an increase of the background intensity.) Our measurement is consistent with the recent scanning electron microscopy study on the Pb equilibrium shape,[20] in which the atomically flat {100} surfaces still persist at $T > 0.95 T_m$. This is in contrast to the Pb(110) surface where the angular profiles undergo a dramatic broadening effect at the roughening transition temperature (~ 415 K).[4]

C. Diffuse intensity as a function of temperature

In Fig. 3 are plots of the ratio of the background intensity to the peak intensity, $R = I_{back}/(I_{peak} - I_{back})$, as a function of temperature for two in-phase conditions ($E=25$ and 55 eV) and two out-of-phase conditions ($E=39$ and 73 eV), where I_{peak} is the total peak intensity. The background intensity I_{back} is subtracted from the total peak intensity before calculating the ratio. The peak intensities at the two in-phase conditions have been corrected for the shifting. For the in-phase diffraction conditions, the ratio R remains a very small constant value below 540 K. This result indicates that the thermal diffuse scattering is undetectable at these diffraction conditions.
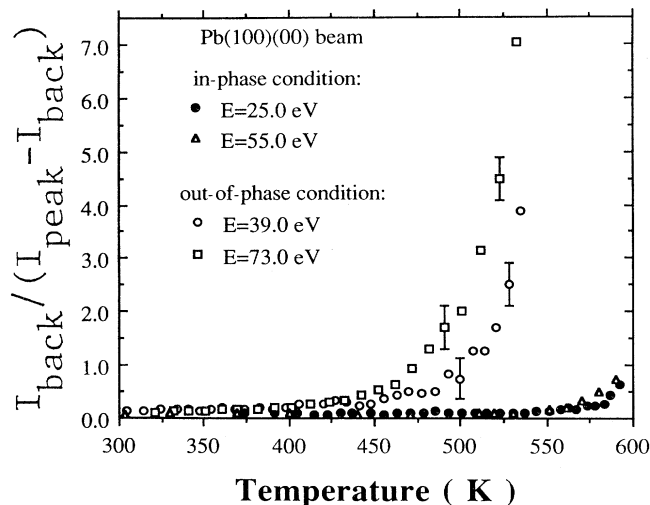

FIG. 3. The ratio of the background intensity to the peak intensity, $R = I_{back}/(I_{peak} - I_{back})$, is plotted as a function of temperature for the in-phase and out-of-phase conditions, where I_{peak} is the total peak intensity. The background intensity I_{back} has been subtracted from the total peak intensity before taking the ratio.

1. Liquidlike disordering at $T > 570$ K

As shown in Fig. 3, R clearly increases at the temperature ~ 570 K for $E=25$ and 55 eV. This is interpreted as a sign of the possible existence of disordering (liquidlike) in the surface where the top layers of atoms become disordered and give a non-Bragg type of atomic scattering. The fact that the peak intensity still persists at a temperature very close to the bulk melting temperature suggests a much weaker disordering involving a thinner layer of surface atoms as compared to that of the Pb(110) surface in which the peak intensity diminishes more quickly at the transition temperature.[2,4,5]

2. Generation of high density vacancies at $480 < T < 540$ K

Between 480 and 540 K, the ratio R for the out-of-phase conditions increases dramatically while R remains a small constant value at the in-phase conditions. The fact that the background increases only for the out-of-phase conditions but not for the in-phase conditions is a typical diffraction characteristic for a surface containing vacancies.[19] Without taking into account the instrumental broadening, the kinematic diffraction intensity from a two-dimensional surface (AAA stacking) containing a vacancy concentration of n is given by[19]

$$I_0(\mathbf{S}) \propto e^{-2M}\{2n(1-n)[1-\cos S_\perp t]$$
$$+(2\pi/a)^2[1-2n(1-n)(1-\cos S_\perp t)]$$
$$\times \delta(\mathbf{S}_\parallel - \mathbf{G}_{hk})\} , \qquad (1)$$

where $\mathbf{S}=(\mathbf{S}_\parallel, \mathbf{S}_\perp)$ is the momentum transfer with the components $\mathbf{S}_\parallel$ and $\mathbf{S}_\perp$ parallel and perpendicular to the surface, respectively; t is the single step height and a is the surface lattice constant in the square unit mesh. $2M$ is the Debye-Waller factor. The intensity given by Eq. (1) contains the δ-function term which describes the peak intensity, and the constant background intensity term which is a result of the destructive interference between the first and second layers of atoms at the vacancies. [For $ABAB$ stacking surface, the result is slightly different from Eq. (1) in the term of the background intensity which is not constant but slowly varies throughout the Brillouin zone.] The background intensity vanishes at the in-phase condition of $S_\perp t = 2m\pi$, but reaches its maximum value at the out-of-phase condition of $S_\perp t = (2m-1)\pi$, where m is an integer.

Recently, the HRLEED study on the Ni(110) surface[21] has shown an increased ratio of the background to peak intensities as a function of temperature at the in-phase condition. This was interpreted as the generation of the substantial vacancies. This effect, if correct, can only be attributed to the structural deformation (or relaxation) near the vacancy. Without relaxation, the vacancy scattering should not give an increase in the background intensity at the in-phase condition due to the interference effect. Reference 22 did not include the coherent scattering contribution from the second layer atoms at the vacancies and therefore cannot predict such an interference behavior[22] which is observed in our experiment.

Equation (1) describes quantitatively the increase of the background intensity due to the generation of surface vacancies but does not explain the temperature dependence of R for the different out-of-phase diffraction conditions shown in Fig. 3. In order to explain the energy dependence of R, we consider the one-phonon scattering effect in the diffraction. In general, the one-phonon scattering intensity can be expressed as[23]

$$I_1(\mathbf{S}) = e^{-2M} \sum_{m,m'} [\langle (\mathbf{S} \cdot \mathbf{u}_m)(\mathbf{S} \cdot \mathbf{u}_{m'}) \rangle] \exp[i\mathbf{S} \cdot (\mathbf{R}_m - \mathbf{R}_{m'})]$$

$$= N^{-1} \sum_{\mu, q_{\parallel}} \langle |\mathbf{S} \cdot \mathbf{u}_{\mu, q_{\parallel}}|^2 \rangle I_0(\mathbf{S} - \mathbf{q}_{\parallel}) , \qquad (2)$$

where $\mathbf{R}_m$ represents the atomic position vector in a rigid surface and $\mathbf{u}_m$ is the corresponding atomic vibrational amplitude. $\mathbf{q}_{\parallel}$ stands for the phonon wave vector parallel to the surface and μ denotes an additional index differentiating between the various phonon modes having

the same $\mathbf{q}_{\parallel}$. The intensity $I_0(\mathbf{S})$ in Eq. (2) represents the zero-phonon diffraction contribution, i.e., $I_0(\mathbf{S}) = e^{-2M} \sum \exp[i\mathbf{S} \cdot (\mathbf{R}_m - \mathbf{R}_{m'})]$, which in our case is given by Eq. (1). N is the total number of atoms in the crystal. $\mathbf{u}_{\mu, q_{\parallel}}$ represents the vibrational amplitude of the phonon mode $(\mu, \mathbf{q}_{\parallel})$ and satisfies

$$\mathbf{u}_m = N^{-1/2} \sum_{\mu, q_{\parallel}} \mathbf{u}_{\mu, q_{\parallel}} \exp(-i\mathbf{q}_{\parallel} \cdot \mathbf{R}_m)$$

and

$$N^{-1} \sum_{\mu, q_{\parallel}} \langle |\mathbf{S} \cdot \mathbf{u}_{\mu, q_{\parallel}}|^2 \rangle = \langle [\mathbf{S} \cdot \mathbf{u}_m]^2 \rangle . \qquad (3)$$

Inserting Eq. (1) into Eq. (2) and using the identity Eq. (3), we can easily show that when the one-phonon effect is included in the calculation for the specular beam, the intensity is modified to give

$$I(\mathbf{S}) = I_0(\mathbf{S}) + I_1(\mathbf{S})$$

$$\propto e^{-2M} \{ (2\pi/a)^2 [1 - 2n(1-n)(1 - \cos\mathbf{S}_{\perp}t)] \delta(\mathbf{S}_{\parallel})$$

$$+ 2n(1-n)(1 - \cos\mathbf{S}_{\perp}t)(1 + S_{\perp}^2 \langle u_{\perp}^2 \rangle) \} + I'_1(\mathbf{S}_{\parallel}) , \qquad (4)$$

where $I'_l(\mathbf{S}_{\parallel}) \propto e^{-2M} S^2 k_B T / |\mathbf{S}_{\parallel}|$ is the conventional one-phonon diffraction intensity[23,24] and $\langle u_{\perp}^2 \rangle$ is the mean square vertical vibrational amplitude. For $S_{\perp}t = 2m\pi$, $1 - \cos S_{\perp}t = 0$, $I'_1(\mathbf{S}_{\parallel})$ manifests itself as the diffuse background intensity at these in-phase diffraction conditions. Experimentally, as shown in Fig. 3, the background intensity is undetectable at all temperatures below the disordering temperature of 550 K and all the angular profiles measured for the in-phase diffraction show no increase of the diffuse intensity. We therefore conclude that the contribution of $I'_1(\mathbf{S}_{\parallel})$ is negligibly small. However, the one-phonon contribution has a dramatic effect on the background intensity for the out-of-phase diffraction. The background is increased by a factor of $(1 + S_{\perp}^2 \langle u_{\perp}^2 \rangle)$. As seen in Eq. (4), this enhancement of the background intensity only exists when the surface contains vacancies. This peculiar but very interesting effect increases the sensitivity of the measurement of the vacancy concentration. The detailed study on this defect-enhanced thermal scattering effect will be published elsewhere.[25]

The ratio R can be determined from Eq. (4):

$$R \propto \begin{cases} 0 & \text{for the in-phase condition} \\ [(2n-1)^{-2} - 1](1 + S_{\perp}^2 \langle u_{\perp}^2 \rangle) & \text{for the out-of-phase condition ,} \end{cases} \qquad (5)$$

where $S_{\perp}^2 \langle u_{\perp}^2 \rangle = 2M$ is proportional to both energy E and $\langle u_{\perp}^2 \rangle$. The mean square vibrational amplitude can be determined experimentally from the Bragg intensity decay (we chose the corrected intensity at $E = 55.0$ eV shown in Fig. 2 as the solid curve, in which the multiple scattering effect is not significant). The only unknown parameter in Eq. (5) is the vacancy concentration n. According to Eq. (5), $R / (1 + S_{\perp}^2 \langle u_{\perp}^2 \rangle) \propto (2n-1)^{-2} - 1$ does not depend on energy but only on vacancy concentration n. Figure 4 shows the measured R divided by the factor $(1 + S_{\perp}^2 \langle u_{\perp}^2 \rangle)$ at the respective out-of-phase energies of 39 and 73 eV. It appears that Eq. (5) describes quite well the experimental results. Both out-of-phase diffraction conditions give the same temperature dependence for $R / (1 + S_{\perp}^2 \langle u_{\perp}^2 \rangle)$. The vacancy concentration can be extracted from Fig. 4. The relative vacancy concentration increases $(20 \pm 5)\%$ from room temperature to 530 K. This high density of vacancies which can substantially lower the surface free energy may be responsible for the liquidlike disordering of the surface. This is in contrast
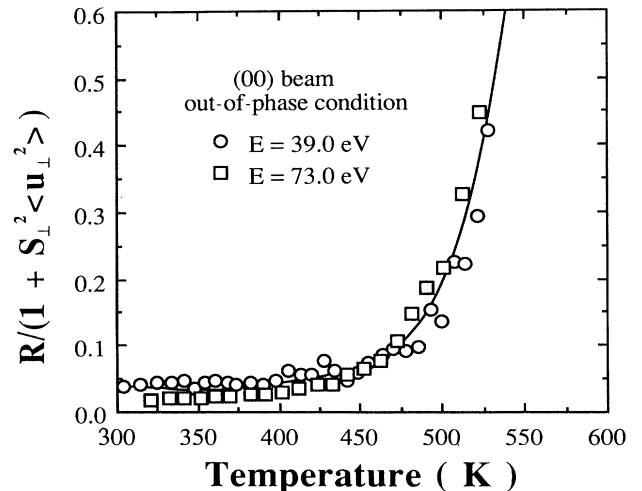

FIG. 4. We plot the temperature dependence of the ratio R divided by the factor $(1 + S_{\perp}^2 \langle u_{\perp}^2 \rangle)$ at two different out-of-phase conditions. The solid curve is a guideline.

to the Pb(110) case where a premelting of the surface is preceded by a multilayer rough phase.

IV. DISCUSSION

Theoretical description of the instabilities in (100) metal surfaces has been very scarce. For reasons similar to those for the (110) case, lattice dynamics calculations[12] which do not include the existence of steps or vacancies are inadequate for the prediction of surface premelting phenomena. The only existing molecular-dynamics simulation work which described the (100) face of a crystal is based on a Lennard-Jones potential.[6] The results are nevertheless stimulating. A steep drop of atom population of the surface layer is observed well below the bulk melting temperature. Accompanied with the drop of the surface population, a steep rise in the surface stress is seen. The surface atomic correlation then dramatically changes into a two-dimensional liquidlike structure. It is hoped that the present experiment can stimulate more theoretical studies, especially of the molecular-dynamics type.

[1]J. W. Frenken and J. F. van der Veen, Phys. Rev. Lett. **54**, 134 (1985).

[2]K. C. Prince, U. Breuer, and H. P. Bronzel, Phys. Rev. Lett. **60**, 1146 (1988).

[3]P. H. Fuoss, L. J. Norton, and S. Brennan, Phys. Rev. Lett. **60**, 2046 (1988).

[4]H.-N. Yang, T.-M. Lu, and G.-C. Wang, Phys. Rev. Lett. **63**, 1621 (1989).

[5]A. Pavlovska and E. Bauer, Appl. Phys. A **51**, 172 (1990).

[6]J. Q. Broughton and G. H. Gilmer, J. Chem. Phys. **79**, 5105 (1983); J. Q. Broughton and L. V. Woodcock, J. Phys. C **11**, 2743 (1979).

[7]V. Rosato, G. Ciccotti, and V. Pontikis, Phys. Rev. B **33**, 1860 (1986).

[8]P. Stoltze, J. K. Norskov, and U. Landman, Phys. Rev. Lett. **61**, 440 (1988); E. T. Chen, R. N. Barnett, and U. Landman, Phys. Rev. B **41**, 439 (1990).

[9]P. Carnevali, F. Ercolessi, and E. Tosatti, Phys. Rev. B **36**, 6701 (1987).

[10]J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).

[11]J. D. Weeks, in *Ordering of Strongly Fluctuating Condensed Matter Systems,* edited by T. Riste (Plenum, New York, 1980), p. 293.

[12]L. Pietronero and E. Tosatti, Solid State Commun. **32**, 255 (1979); C. S. Jayanthi, E. Tosatti, and L. Pietronero, Phys. Rev. B **31**, 3456 (1985).

[13]B. Pluis, A. W. Denier van der Gon, and J. F. van der Veen, Surf. Sci. **239**, 265 (1990).

[14]S. G. J. Mochrie, D. M. Zehner, B. M. Ocko, and D. Gibbs, Phys. Rev. Lett. **64**, 2925 (1990).

[15]Y. Cao and E. Conrad, Phys. Rev. Lett. **65**, 2808 (1990).

[16]U. Scheithauer, G. Meyer, and M. Henzler, Surf. Sci. **178**, 441 (1986).

[17]T.-M. Lu and M. G. Lagally, Surf. Sci. **99**, 695 (1982).

[18]T.-M. Lu and M. G. Lagally, Surf. Sci. **120**, 147 (1982).

[19]J. M. Pimbley and T.-M. Lu, Surf. Sci. **139**, 360 (1984).

[20]A. Pavlovska, K. Faulian, and E. Bauer, Surf. Sci. **221**, 233 (1989).

[21]Y. Cao and E. Conrad, Phys. Rev. Lett. **64**, 447 (1990).

[22]John M. Cowley, *Diffraction Physics* (North-Holland, Amsterdam, 1984), p. 144.

[23]D. L. Huber, Phys. Rev. **153**, 772 (1966).

[24]J. T. McKinney, E. R. Jones, and M. B. Webb, Phys. Rev. **160**, 523 (1967).

[25]H.-N. Yang and T.-M. Lu (unpublished).