Double-Sine-Gordon Solitons: A Model for Misfit Dislocations on the Au(111) Reconstructed Surface

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We demonstrate that the reconstruction of the Au(111) surface can be interpreted in terms of a new type of misfit dislocations, namely, double-sine-Gordon-type dislocations. First, we motivate the applicability of this class of solitons to the reconstruction problem. Second, we describe the procedure we have used to construct the model unit cell containing the double-sine-Gordon quasi one-dimensional dislocations. Finally, comparison with experimental He-scattering results is established by computation of the corresponding diffraction pattern using a hard corrugated wall and the eikonal approximation.

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Investigations of the structure of clean and adsorbate-covered single-crystal surfaces of metals and semiconductors have revealed that under certain conditions the topmost layer incorporates some degree of mismatch with respect to the underlying bulk structure.[1-3] In some cases the mismatch is accommodated into commensurate structures, in other cases through the creation of misfit dislocations or some degree of disorder.[1-3] In the case of clean surfaces such reconstructions have been observed on the (100) surfaces of Ir, Pt, Au, Cr, Mo, and W, the (110) surfaces of Ir, Pt, and Au, and the (111) surface of Au.[2] A large number of investigations of the structure of adlayers, both metallic and nonmetallic, have reported similar findings.[1-3] These results have led to an extensive revival of the Frank and van der Merwe analysis of solitonlike misfit dislocations.[4] Most of the work reported in the past, both theoretical and experimental, has dealt mainly with the nature of the critical behavior of incipient phase transitions, especially the commensurate-incommensurate, melting, and pinning-depinning transitions,[1,3] as well as transport properties of charge-density waves.[2] It was only very recently that direct experimental investigations of the structural properties of solitons have been reported.

Harten *et al.*[5] reported diffraction measurements on the reconstructed (111) surface of Au using a He-beam scattering apparatus with high angular and energy resolution. They interpreted the diffraction pattern as a manifestation of quasi one-dimensional sine-Gordon (SG) solitonlike misfit structures. However, instead of fitting an SG solitonlike atomic arrangement to the diffraction data, they accounted for the presence of the solitonlike structures by a model containing equivalent Gaussian corrugations with full width at half maxima equal to the soliton width. We believe that the adoption of such a procedure was dictated by the inability of the SG soliton model to justify *a priori* the unequal areas of the regions with stacking A (hcp-like) and C (fcc-like), although it can account for the extra packing of half an atom per soliton dislocation with incommensurability 2.

The purpose of the present paper is to introduce a different soliton model which provides a faithful interpretation of the diffraction data on the reconstructed Au(111) surface. This model incorporates the new concept of competing sites in addition to that of competing periodicities and thus can account *a priori* for the first observation cited above. The realization of this model is based on *double-sine-Gordon (DSG)-like*[6] soliton dislocation. This class of solitons has recently found diverse speculative applications in many fields of physics such as condensed matter,[6] nonlinear optics,[6] and particle physics.[6] The interest in this type of solitons is due to the fact that it possesses internal dynamical structure.[6]

It is well known[7] that surfaces with hexagonal structure have two equivalent adatom sites which are conventionally labeled A and C; A is associated with the hcp stacking and C with fcc stacking. The two sites are not energetically degenerate when one type of stacking is favored. In the case of the Au(111) surface layer the C site should be favored if a continuation of the bulk structure occurs. However, it has been proposed[8] that a redistribution of sp electrons in the surface layer may favor a reduction of the interatomic separation from the bulk value. The competition between occupying the C sites and reducing the mean interatomic separation in the surface layer is resolved by accommodating both A and C sites, thus reducing the average interatomic spacing through the concept of defectability, i.e., the creation of local defects or, in this case, solitons. In the case of the fcc (111) surfaces the topology of the underlying substrate potential is such that the minimum-energy path for the transition from one site type to the other is effected across the shared bridge site. Potential energy minima are located at the A and C sites, while a saddle point is found at the bridge site. The resulting zigzag shape of the underlying potential can be unfolded into a one-dimensional potential. The nondegeneracy of the A- and C-site energy minima is suggestive of a DSG-like

substrate potential that can be written

$$V_{\mathrm{DSG}}(x)=\frac{W}{2}\frac{16}{(R+4)^2}\left\{R\left[1-\cos\left(\frac{2\pi x}{a}\right)\right]+1-\cos\left(\frac{4\pi x}{a}\right)\right\},$$

where W is the peak-to-peak amplitude, a is the potential periodicity, and $0.0\leq R\leq 4.0$. The range of the parameter R defined here maintains a potential maximum of W and an absolute minimum of zero at the C site, while the A-site energy varies from zero at $R=0$ to a potential maximum of energy W at $R=4.0$. The former limit corresponds to an incommensurability $p=2$ SG system.[2] The Hamiltonian of the corresponding finite Frenkel-Kontorova–type chain is

$$H=\frac{\mu}{2}\sum_{i=0}^{N}[x_{i+1}-x_i-(b-a)]^2+\frac{W}{2}\frac{16}{(4+R)^2}\sum_{i=0}^{N}\left\{R\left[1-\cos\left(\frac{2\pi x_i}{a}\right)\right]+1-\cos\left(\frac{4\pi x_i}{a}\right)\right\},$$

where x_i is the displacement of the ith particle from the bottom of the ith C well, b and μ are the equilibrium interparticle spacing and the elastic constant of the surface layer, respectively, and N is the number of particles comprising the chain. This model is represented schematically in Fig. 1(a). By substitution of $u_i=x_i/a$, H becomes

$$H=\frac{\mu a^2}{2}\sum_{i=0}^{N}\left[u_{i+1}-u_i-\frac{1}{p_0}\right]^2+\frac{W}{2}\frac{16}{(4+R)^2}\sum_{i=0}^{N}\{R[1-\cos(2\pi u_i)]+1-\cos(4\pi u_i)\},$$

where $p_0=a/(b-a)$. The corresponding equations of motion are

$$u_{i+1}-2u_i+u_{i-1}=(\pi/l_0)^2[R\sin(2\pi u_i)+2\sin(4\pi u_i)],$$

where $l_0^2=\mu a^2/2W$. The continuum limit of this equation has stable solutions of the form

$$\tan(\pi u)=\left(1+\frac{4}{R}\right)^{1/2}\operatorname{csch}\left(\frac{4\pi n}{(R+4)^{1/2}l_0}\right).$$

This solution can be viewed as a configuration of two bound π solitons, each with an effective length of $l_0/2$, and center-to-center separation $L(l_0,R)$. For $R\ll 1.0$, $L\simeq(l_0/4\pi)\ln(1/R)$.

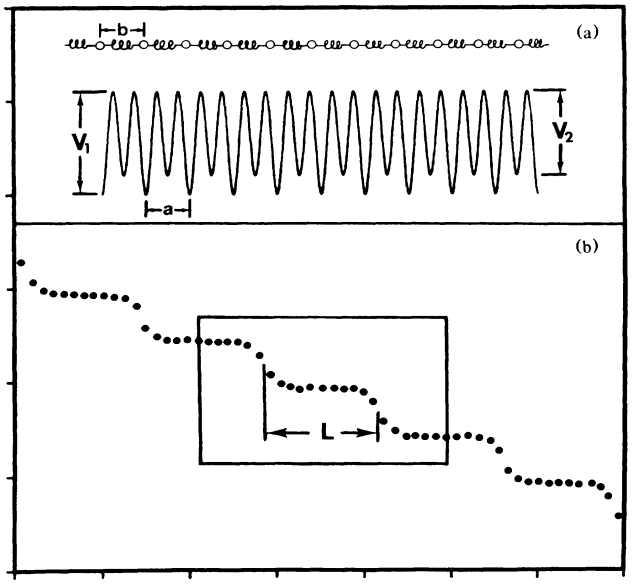

FIG. 1. (a) A schematic diagram of a DSG-like Frenkel-Kontorova model where $V_1=W$ and $V_2=(1-R)W$. (b) Profile of a DSG soliton chain showing the displacement u_n of the nth particle from the nth C-type well. Inset: Individual DSG soliton.

In fitting the He-diffraction data to the DSG model we have adopted the following procedure. We fixed the mismatch to the value reported by Harten *et al.*,[5] namely, $b/a=\frac{22}{23}$. The choice of the parameters of the DSG model was based on the information given in Ref. 5; namely, $l_0\simeq 8a$ and $R=0.01$ were found to agree with a DSG subsoliton size of about $4a\simeq 12$ Å and a ratio of A to C regions of 0.70. We used molecular-dynamics procedures outlined in earlier publications[9,10] to determine the equilibrium metastable configurations of a harmonic chain with DSG solitons. A typical equilibrium configuration, u_i, containing DSG solitons, is shown in Fig. 1(b), where the dots indicate the positions of the atomic centers. Subsequently, we used the configuration of the central soliton in the relaxed chain configuration to construct the $(23\times\sqrt{3})$ unit cell of the reconstructed Au(111) surface. The equilibrium positions of the particles constituting the DSG soliton were used as the x coordinates of the atomic centers along the ⟨110⟩ direction; the y and z coordinates, along the ⟨112⟩ and surface normal, respectively, were then determined from a hard-sphere stacking model with the interatomic separation of the bulk. However, the y coordinate was reduced by a factor of 0.98 in order to account for the shift of the center spot of the ⟨112⟩ diffraction group to higher K values.[5] In contrast to the isotropic compression of 2% imposed by Harten *et al.*, to account for the shift of the diffraction spots and to obtain a reasonable fit, we interpret the compression to be uniaxial, i.e., along the ⟨112⟩ direction only. A typical planar view of the atomic arrangement is shown in Fig. 2(a). The soliton stacking pattern in the ⟨112⟩ direction is dictated by the doubling

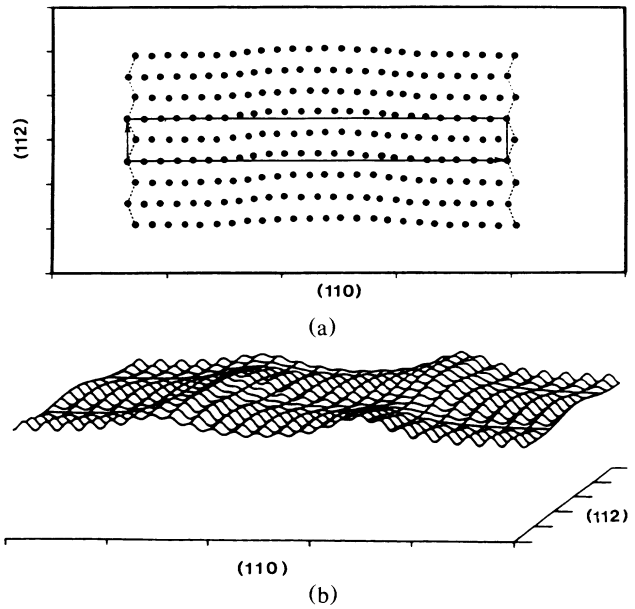

FIG. 2. (a) Planar view of the atomic arrangement involving DSG solitons. Notice the atomic displacements in the ⟨110⟩ and the zigzag stacking of solitons along the ⟨112⟩ directions. (b) Unit-cell corrugation.

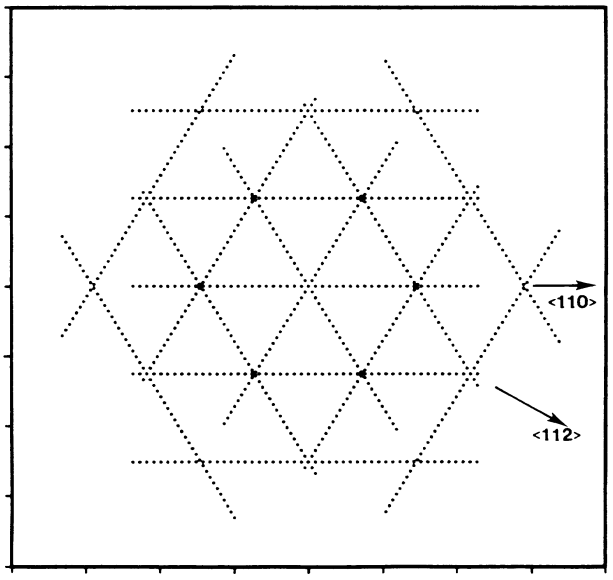

FIG. 3. Reciprocal-lattice view of the superposition of the three equivalent domains.

of periodicity in that direction, which corresponds to having two inequivalent soliton sites in the unit cell, i.e., not connected by a primitive lattice vector of the underlying hexagonal structure. This arrangement results in a zigzaglike pattern along the ⟨112⟩ direction, which is also indicated in Fig. 2(a). The apparent sixfold symmetry manifest in the diffraction spots is generated by the presence of three domains with 120° relative rotations. The last step in simulation of the reconstructed surface was to superimpose Gaussian charge distributions characterized by a width σ and an amplitude A on the atomic-center positions in order to reproduce the associated surface corrugation manifested in the He scattering. The resulting simulation of the unit-cell corrugation is shown in Fig. 2(b). Finally, we computed the atomic-beam diffraction intensities associated with the predicted corrugation using the hard wall and the eikonal approximations.[11] Since the purpose of the present paper is to introduce and motivate the DSG model as a possible candidate for surface misfit dislocations, we opted not to carry out a systematic and thorough search over the parameter space (l_0, R, σ, A) for a best fit to the diffraction data. Instead we simply chose $\sigma = 0.4a$ and $A = 1.5$ in order to reproduce the peak-to-peak atomic corrugation of 0.07 Å cited in Ref. 5. A height of the envelope corrugation of 0.15 Å associated with the soliton was dictated by the hard-sphere model and is in agreement with Harten *et al.* The diffraction intensities computed from the DSG model are given in Table I where they are compared with the experimental values and with the fitted intensities reported for the model of Harten *et al.* Furthermore, in Table I we have identified the observed diffraction peaks in terms of the reciprocal lattice vectors of the new rectangular unit cell. To facilitate further the identification of the diffraction pattern we provide in Fig. 3 a schematic diagram of reciprocal space where we show the superimposed contributions of the three equiv-

TABLE I. Diffraction peaks of reconstructed Au(111) surface.

Peak	Experiment	Intensity DSG	Harten *et al.*
1(1,0)	4.0	7.5	7.4
2(2,0)	26.0	28.0	24.7
3(3,0)	5.5	5.0	5.5
4(4,0)	···	0.2	0.5
5(5,0)	0.5	1.0	0.7
A(24,−1)	1.3	0.8	1.0
B(−24,−1)	1.0	0.8	1.0
C(±1, ∓2)	0.5	0.7	0.5
D(0, ±2)	0.7	1.7	1.2
E(±1, ±2)	0.5	0.5	0.5
F(±22, ±1)	0.2	0.1	0.2
G(±22, ∓1)	0.2	0.05	0.1
H(±22, ∓1)	0.1	0.05	0.1
I(±22, ±1)	0.1	0.05	0.1
J(±1, ±2)	···	···	0.2
K(0, ±2)	2.0	2.4	2.0
L(±1, ∓2)	0.05	···	0.2
M(25,1)	0.9	0.1	0.8
N(−25,1)	0.6	0.08	0.8

alent reconstructed domains. A comparison of this diagram with Fig. 2 of Ref. 9 will prove helpful in the identification. Furthermore, it will underline the uniqueness of the proposed soliton zigzag stacking in the ⟨112⟩ direction, since the orientation of the ⟨112⟩ hexagonal group of diffraction spots can only be reproduced by the proposed stacking.

Finally, we address briefly the implications of the DSG model on the interpretation of the recently measured phonon dispersion for the Au(111) reconstructed surface,[12,13] and we comment on the relevance of the dynamical models proposed to explain the anomalous features observed. First, the radical reduction in surface symmetry from C_{3v} of the fcc (111) surface to C_1 effected by the introduction of the DSG soliton dislocation allows mode mixing among the surface-phonon branches associated with the unreconstructed fcc (111) surface. This mixing may be significant for wavelengths $\geq l_0/4$ along the ⟨110⟩ direction. Moreover, features associated with the unit-cell doubling along the ⟨112⟩ direction should also be manifested in the experimental data. Evidence of the former can be inferred from the appearance of two closely separated branches below the bulk continuum,[12] which seem to merge at wavelengths ≤ 0.8 Å^{-1}. Furthermore, a careful examination of the dispersion curves along the ⟨112⟩ direction reveals an abrupt change in slope at half the Brillouin-zone wave vector which may be a signature for the new Brillouin-zone boundary along that direction. The manifestations of small oscillations associated with the DSG soliton itself, i.e., soliton vibration modes,[14,15] are unfortunately not amenable to the current energy and momentum resolutions of He scattering because of the large unit cell (23 atoms) and the softness of the surface force constants, $\omega_{max} \simeq 6$ meV.

We believe that attempts to use dynamical models based on the unreconstructed configuration symmetry to fit the experimental dispersion curves and identify their polarizations will be misleading; however, such models can be most useful in providing insight into the microscopic origin of the instability in the unreconstructed surface that drives the surface into the soliton dislocation configuration, as has been attempted recently by Jayanthi *et al.*[16]

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