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Analysis of molecular-dynamics simulations of the (111) surface of germanium crystal near its bulk melting temperature

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A molecular-dynamics (MD) simulation of the Ge(111) surface within 2% of the Ge bulk melting temperature T_m has been analyzed statistically, and the results have been applied in a discussion of low-energy electron diffraction (LEED) observations of disordering at Ge(111). MD results indicate that long-range disordering occurs only on laterally compressed model crystals. An analysis of vibrational disorder in regions retaining local crystalline order confirmed the applicability of the Debye-Waller theory to LEED from Ge near T_m. Calculations of the positional pair-correlation function indicated that, in regions where crystalline order is absent, the surface structure is that of a two-dimensional liquid layer with some degree of periodic density modulation.

I. INTRODUCTION

Molecular-dynamics (MD) simulations have an important role in current efforts to understand processes such as disordering and epitaxy at crystal surfaces.[1,2] Since MD is only practicable for small samples, representing at most 10^3 surface atoms, a statistical analysis can be useful in making contact with experiments on macroscopic crystals. In this paper we present a statistical analysis of MD simulations of the (111) surface of germanium crystal at temperatures near its bulk melting temperature.

The application of MD to the Ge(111) surface was prompted by low-energy electron diffraction (LEED) experiments indicating a surface disordering phase transition about 160 K below the bulk melting temperature T_m (1210 K).[3,4] In contrast to diffraction experiments employing penetrating radiation such as x rays, which sample the bulk structure of crystals, the LEED experiment samples only the outermost few atom layers of a crystal.[5] Thus LEED is sensitive to surface long-range order (surface crystalline order). The LEED results for Ge(111) were attributed tentatively to a loss of lateral long-range order in the outermost double layer of the crystal. On the basis of some experimental indications of surface strain, it was suggested that the disordering might be induced by intrinsic lateral compressive stress at the Ge(111) surface at high temperature.[4] Some uncertainties in conclusions from LEED derive from the difficulty in disentangling the effects of long-range disorder from those of the thermal vibrational disorder which is always present.[5] Others derive from the prevalence of multiple scattering in LEED. A tentative conclusion, based on the kinematical (single-scattering) approximation, is that layerlike ordering is maintained up to the outermost double layer, even when the surface is laterally disordered.[4] MD simulations offer a check on these aspects of the interpretation of LEED results.

Our initial attempts to deal with these questions raised by LEED results were based on calculations of the kinematical intensity function $I(\mathbf{K})$ for the disordered crystal ($\mathbf{K}$ denotes the momentum transfer in diffraction). But this approach has the drawback that the $I(\mathbf{K})$'s calculated for a single configuration exhibit many peaks in addition to those associated with the long-range order parallel to the surface. These extra peaks (extra "beams" in the parlance of LEED) derive from quasiperiodic atom displacements normal to the surface, associated apparently with large-amplitude surface phonons. In our experience, a large number ($\gg 10$) of MD configurations must be averaged to smooth out these extra peaks into the thermal diffuse background to the diffraction pattern. Subsequently we found it more rewarding to focus on other statistical measures of order disorder, namely, the distribution of atom displacements from their equilibrium positions and the positional pair-correlation function [the Fourier transform of $I(\mathbf{K})$].

II. MOLECULAR-DYNAMICS SIMULATIONS

In the MD simulations, the Stillinger-Weber (SW) interatomic potential originally developed for Si (Ref. 6) was used. A potential has recently been published that gives a good fit to the structure of amorphous Ge,[7] but we chose to use the SW potential because of the extensive simulation data available on its thermodynamic properties. The Ge crystal was represented by 1440 atoms in slablike arrangement consisting at low temperatures of six (111) atom double layers of the Ge crystal structure. This model provides two (111) surfaces, each with 120 atoms in crystallographically equivalent surface sites. Periodic boundary conditions were applied in the two directions parallel to the slab to eliminate edge effects at the boundaries of the computational cell. The sizes of the cells correspond to the crystal lattice constants at the selected temperatures. These were determined in separate constant-pressure simulations of the bulk crystal (without crystal-vapor interfaces) at zero pressure. Systems with the lateral dimensions contracted relative to the values for zero pressure were also studied, as described below. The initial configurations consisted of atoms placed at the diamond lattice sites, and these were equilibrated for at least 2×10^4 MD time steps, where one time step is 10^{-2} dimensionless time units of the SW potential. MD runs of 4×10^4 time steps were used to obtain statistics. More details on the implementation of the SW potential are provided in Ref. 2. In the first MD runs, the atoms were located at low temperature on the diamond lattice with the Ge lattice constant for zero pressure. These simulations failed to produce any long-range disordering. Subsequently, MD runs were done for a slablike model crystal with the same structure as before except for area compression parallel to the (111) layers. As the SW potential specifically provides zero surface stress at zero Kelvin (and hence very little stress at any temperature) the surface stress corresponding to the compression of the slab represents the stress that might be present in a real crystal. Simulations on models compressed by more than 2% in each direction parallel to the (111) surface produced definite indications of long-range disordering in the outermost double layer.

Examples of instantaneous atom configurations in MD simulations of Ge crystal in thermal equilibrium are shown in Fig. 1. The simulation crystal temperature was $0.98T_m$ where T_m denotes the bulk melting temperature for the SW potential.[8] The atom positions refer to the outermost double layer. The atom positions in an ideal crystal at zero Kelvin are shown for comparison [Fig. 1(a)]. For a 2% compressed crystal [Fig. 1(b)] there is evident short-range disorder due to thermal vibrations of atoms about their equilibrium positions, but except for one lattice defect the long-range order of the atom equilibrium positions is intact. For a 4% compressed crystal [Fig. 1(c)] there is long-range disorder as well as thermal vibrational disorder. The disordered double layer contains "islands" within which the crystalline structure is retained locally, but these are separated by "seas" of disordered Ge atoms. Relative to the underlying layers, the islands are expanded laterally by 3%. For the compressed as well as the uncompressed crystal, the inner double layers retain long-range order. These results are consistent with the suggestion that disordering of Ge(111) is induced by intrinsic lateral compressive stress.

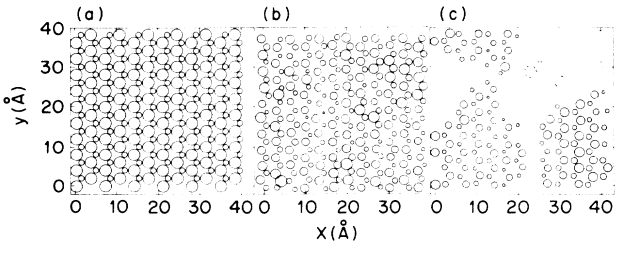

FIG. 1. Atom positions in the outermost double layer of a molecular-dynamics simulation of the (111) surface of Ge crystal. The centers of the circles correspond to the lateral positions of atoms. The sizes of the circles indicate the surface-normal positions, with the largest circle corresponding to the atom farthest from the bulk crystal. (a) An ideal crystal at zero Kelvin. (b) A model crystal compressed by 2% in both lateral directions. (c) A model crystal compressed by 4% in both lateral directions. Heavy circles indicate atoms in regions of crystalline order.

III. THERMAL VIBRATIONAL DISORDER

In diffraction experiments on crystals, such as x-ray diffraction and LEED, the intensity of diffracted beams tends to decline with increasing crystal temperature as a result of the thermal vibrational disorder. A theoretical description of the temperature effect (Debye-Waller theory) was early derived in the context of x-ray diffraction,[9] and has been applied in a modified form to LEED as well.[5] Generally the ratio of the peak intensity of a diffraction beam from a crystal at zero Kelvin to the peak intensity at temperature T is called the Debye-Waller (DW) factor. According to the Debye-Waller theory for an elemental crystal, as derived for x rays, the DW factor has the expression $\exp(-2M'T)$, where M' is independent of T and is related to the displacements $\mathbf{u}$ of atoms from their equilibrium positions and to the momentum transfer in diffraction, $\mathbf{K}$, by

$$2M' = \langle (\mathbf{K}\cdot\mathbf{u})^2 \rangle / T \ , \tag{1}$$

where the angle brackets denote a time average.

Though the condition of kinematical (single scattering) theory assumed in the derivation of Eq. (1) is not fulfilled in the case of LEED, Eq. (1) has nevertheless proved applicable to LEED for long-range ordered surfaces, as long as the displacements $\mathbf{u}$ are taken to be those of atoms in the outermost few atom layers. For these atoms, the average square of the displacement in the direction normal to the surface of a monatomic crystal is larger than the average square displacement parallel to the surface, and is generally estimated to be about twice the corresponding value for atoms in the bulk crystal. One expects, in conformity with this estimate of surface-normal displacement, that the peak intensity of the (00) LEED beam (specular) should vary with T like a DW factor with a value of M' about twice the value corresponding to bulk atom displacements. This "normal" DW factor has been observed in LEED experiments on long-range ordered crystal surfaces at temperatures up to about half the bulk melting temperature.[5,10] We do not know of any comparable observations on crystals nearer to the bulk melting temperature.

In the interpretation of LEED experiments focusing on thermal long-range disordering, it is usual to remove the effect of vibrational disordering by dividing by an estimated normal DW factor. The assumptions are that the normal DW factor applies to diffraction from regions in which crystalline order persists even in the presence of long-range disordering in other regions, and that it applies for crystal temperatures above as well as below the disordering transition temperature. These assumptions are tested here, using MD results for the Ge(111) surface near its bulk melting temperature.

The key assumption in the DW theory pertains to the time-average distribution of displacements of atoms in a given direction from their equilibrium positions. It is assumed that this distribution is Gaussian. For a Gaussian distribution, the time average over factors representing the dephasing effect of thermal vibrations has the form indicated in Eq. (1).

In order to test the Gaussian-distribution assumption, we assume that the instantaneous distribution of atom displacements from different but crystallographically equivalent lattice sites is the same as the distribution of displacements from one such site at different times. We have examined these displacements of atoms in the outermost three double layers of one configuration of each of the slabs with respective compressions of 2% and 4%. In the case of the 4% compressed slab, the outermost double layer was disordered as shown in Fig. 1(c). Of the atoms making up the outermost double layer, only those belonging to ordered regions [heavy circles, Fig. 1(c)] were included.

An indication of the degree to which the distribution of displacements of atoms in a given layer resembles a Gaussian distribution is provided by quantile-quantile plots[11] such as illustrated in Fig. 2. The quantile-quantile plot is the plot of the quantiles (i.e., ordered observations) of the distribution under examination against the corresponding quantiles (i.e., theoretically expected ordered values for a sample of the same size) from the standard Gaussian distribution (normal probability plot). If the distribution were Gaussian, the plot would be a straight line. The value of the correlation coefficient from this plot can be used as a measure of its linearity. The maximum value of unity corresponds precisely to a Gaussian distribution, while low values indicate that the distribution under examination is not Gaussian. A published table[12] can be used along with the value of the correlation coefficient and the sample size to test the null hypothesis that the distribution is Gaussian. The significance level read from the table gives the probability of obtaining a correlation coefficient this small or smaller, when the distribution is in fact Gaussian. A significance level in excess of 0.05 is commonly accepted as indicating that the distribution under examination is Gaussian. For sample size 100, this significance level corresponds to a correlation coefficient of 0.987.

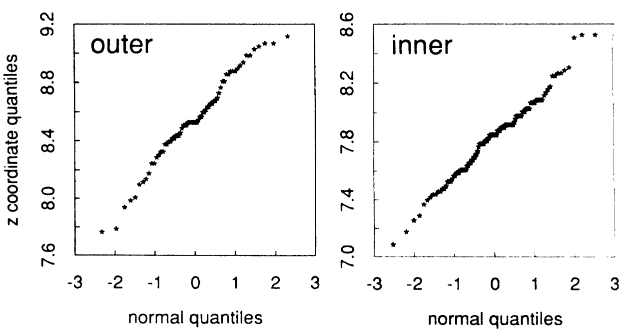

FIG. 2. Quantile-quantile plots indicating the extent to which distributions of atom displacements resemble the Gaussian distribution. The plots refer to displacements in the direction normal to the (111) surface, for the inner and outer layers shown in Fig. 1(c).

The plots shown in Fig. 2 refer to the distribution expected intuitively to deviate most from the Gaussian one, namely, that of the surface-normal coordinates of atoms belonging to the outermost double layer of the most disordered (4% compressed) slab. They indicate that a nearly Gaussian distribution of coordinates is obtained despite long-range disordering in the same double layer, at a temperature within 2% of the bulk melting temperature.

A summary of calculated correlation coefficients is presented in Fig. 3. The sample size was 120 except for the outermost double layer of the 4% compressed slab where it was between 50 and 100. The surface-parallel displacements were calculated for the x direction, relative to mean values of the x coordinates of atoms in rows running parallel to the y axis. The values of the correlation coefficients indicate Gaussian distributions, with one exception only. In the exceptional case, for surface-parallel displacements in the second atom layer of the 4% compressed slab, the low value is due to outlying points corresponding to atoms at the boundary between ordered and disordered regions. Also shown in Fig. 3 are the average-square displacements normal to and parallel to the (111) surface. The root-mean-square (rms) surface-normal displacements are larger than the average rms surface-parallel ones, and are about $\sqrt{2}$ times as large for the outermost layer as for the bulk (as represented by the innermost layer). This picture is similar to that for crys-

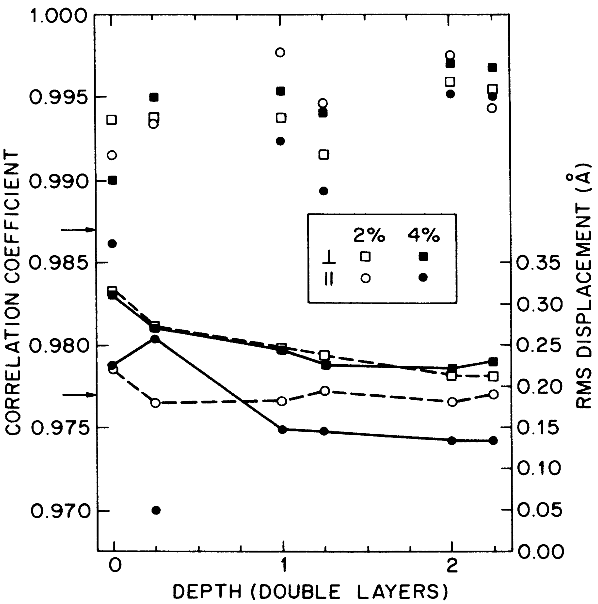

FIG. 3. Statistical quantities pertaining to the distributions of atom displacements in the outermost six layers of model crystals. 2% and 4% indicate compression, and refer to the models illustrated in Figs. 1(b) and 1(c), respectively. $\perp$ and $\parallel$ denote displacements normal and parallel to the (111) surface. Arrows at the left scale indicate values of correlation coefficient corresponding to the 0.05 significance level for sample size 100 (upper arrow) and 50. Data points connected by lines refer to the root-mean-square displacement of atoms (right scale).

tal surfaces at low temperature.[5,10]

Our results show that in MD simulations of Ge(111) surface, the key assumption of the DW theory holds good even in the presence of long-range disordering and even at temperatures very close to the melting temperature of the bulk crystal. That is, the distributions of thermal displacements of atoms resemble a Gaussian distribution according to a standard statistical criterion. The MD simulations give no indication of a gross failure of the DW theory. They tend to justify the procedure of dividing out the effect of thermal vibrational disorder using a normal DW factor.

IV. LONG-RANGE DISORDER

While configuration plots such as those presented in Fig. 1 clearly show the presence of long-range disorder, the nature of the disorder is not immediately apparent from these plots. What is needed is an impression of the "average" surroundings of an atom. This is provided by the positional pair-correlation function (PCF).[13] The positional PCF $G(\mathbf{R})$ is proportional to the probability that two atom centers are separated from each other by the position vector $\mathbf{R}$.

For a given configuration, the positional PCF $G(\mathbf{R})$ was calculated for values of $R \equiv |\mathbf{R}|$ up to a maximum value $R_{\max}$. The calculation was done with respect to temporary origins at atoms belonging to the outermost double layer and within specific lateral sampling regions. The lateral sampling region associated, e.g., with a region of the surface exhibiting crystalline order is delimited so that no atom within it lies closer than $R_{\max}$ to the edge of the ordered region. Spherical polar coordinates (R,θ,ϕ) were used. For an origin at a particular atom, the number of atoms within the volume element ΔV_j corresponding to the jth value $\mathbf{R}_j$ out of a discrete set of coordinate values was determined, and this number was averaged over the sampling region and divided by ΔV_j to evaluate $G(\mathbf{R}_j)$.

The results of the calculation of the positional PCF may be displayed as separate plots of the angular PCF and the radial PCF obtained by integrating over radial and angular coordinates, respectively. Figure 4 shows results for a configuration with long-range disorder at the surface of a 4% compressed slab. It corresponds to Fig. 1(c). In Fig. 4, the angular PCF is presented by "inward" and "outward" stereographic projections. The inward projection, e.g., describes the environment of a surface atom to its bulk-crystal side. For an appropriate visual rendering of the enhancement of $G(\mathbf{R}_j)$ where more than one atom lay within the corresponding volume element, the jitter technique was used to displace the plotted points on the unit sphere.

As shown in Fig. 4, the radial PCF's for the ordered and disordered regions are very similar to each other. For the disordered region relative to the ordered one, there is a slight broadening of the peak at a radius near the Ge—Ge bond length.

The angular PCF's (Fig. 4) reveal some properties of the disordering that are not apparent in configuration plots such as Fig. 1(c). Both the inward and outward projections for the disordered region have a predominantly annular distribution of density consistent with the presence of a two-dimensional liquid layer. The integrity

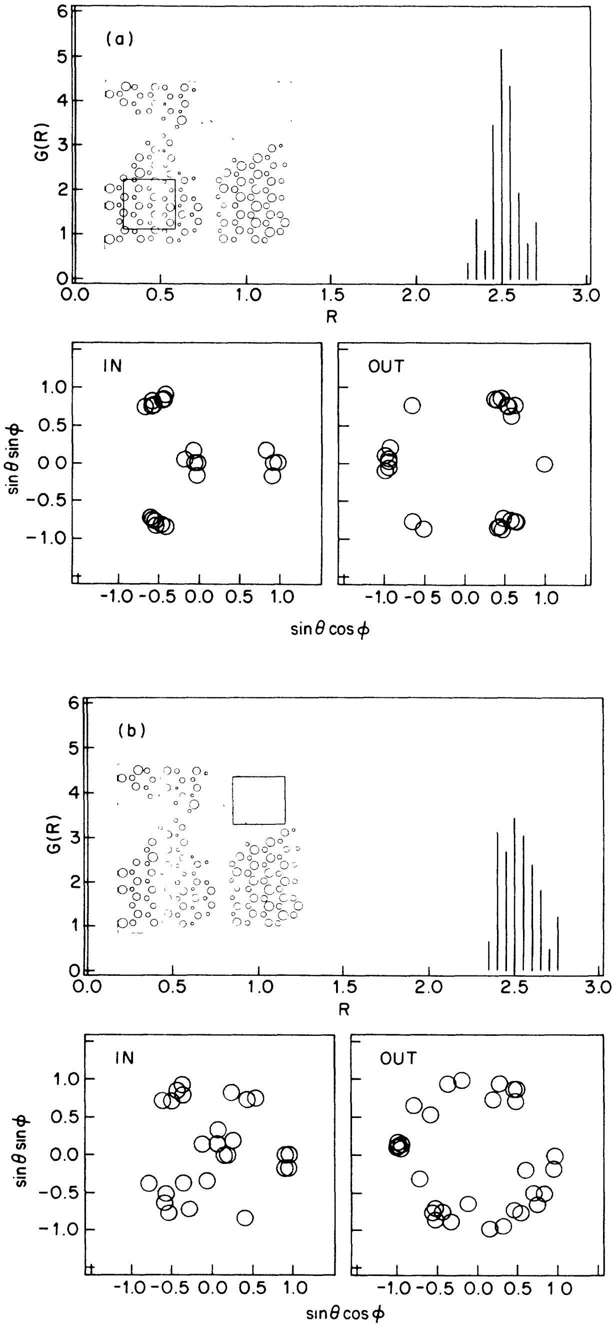

FIG. 4. Pair-correlation functions (PCF's) calculated for (a) ordered and (b) disordered surface regions of the model in Fig. 1(c). For each region, the radial PCF (top) and the inward (in) and outward (out) stereographic projections of the angular PCF's (bottom) are shown. The respective sampling regions are shown by insets. The calculations were done with $R_{\max}=2.8$ Å, and with volume elements corresponding to the following increments of spherical polar coordinates: $\Delta R=0.05$ Å, $\Delta\theta=\Delta\phi=10°$. The angular amplitude of jitter was ±2.5°.

of the outermost atom double layer is evidently preserved. Superimposed on the annular density, however, there is extra density at trigonally related positions and also at the center of the inward projection. These superposed densities resemble to some degree the densities found for the ordered region. Thus the disordered surface represented by MD has the layerlike structure of a two-dimensional liquid, modulated with the periodicity of the underlying crystal. A measure of the extent to which layerlike ordering is preserved is provided by calculations like those on the ordered regions (Sec. III). Relative to the outermost double layer of the ordered crystal, the mean surface-normal coordinate of the corresponding atoms in the disordered regions is shifted inwards by 0.13 Å or 4% of a double-layer spacing. The surface-normal displacements have a Gaussian distribution as indicated by a correlation coefficient of 0.990. The root-mean-square displacement of the atoms is 0.59 Å. These figures indicate that layerlike ordering persists to some extent in the disordered region, but not to the extent required to support an interpretation of the LEED observations[3,4] by a surface-melting transition.[4]

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