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X-ray study of the oxidation of liquid-gallium surfaces

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The oxidation of liquid-gallium surfaces has been investigated with surface x-ray scattering techniques. By exposing the liquid-metal surface at room temperature to doses on the order of 180 L of oxygen where 1 $\mathrm{L}=10^{-6}$ Torr s, a gallium oxide film with a well-defined thickness of ~5 Å readily forms. The oxide thickness and roughness of the liquid/oxide and oxide/vapor interfaces do not change with oxygen dosage up to 1600 L nor with temperature up to 573 K. This is in contrast to what is observed for the bare liquid-Ga surface, which is roughened significantly by thermally excited capillary waves with temperatures up to only 443 K. This is a good indication that the oxide layer provides rigidity to the liquid surface and is likely a solid; grazing-incidence measurements suggest that the film is amorphous or poorly crystallized. Based on comparisons with known crystal structures, models are suggested for the atomic arrangements in the gallium oxide layer and its interface with the underlying liquid. [S0163-1829(97)03815-0]

Oxidation and corrosion of crystalline metal surfaces have been extensively studied for many years, leading to a good understanding of the basic metallurgical processes and the corresponding surface chemistry and physics.[1] The control of oxidation, which follows from improved understanding of the microscopic processes at the interfaces and the oxide films, has the potential for improving both the chemical and physical properties of the material. Aluminum is a frequently cited example, where enhanced corrosion resistance arises from the natural formation of an inert oxide layer on its free surface.[2] The study of liquid-metal surface oxidation is of particular importance since, on the one hand, these surfaces are highly reactive and thus readily oxidize even under high vacuum conditions and, on the other hand, such surfaces are involved in many key processing technologies (e.g., smelting and refining of ores, casting, brazing, alloying, and zone melting[3]) and have a profound influence on them. For example, it has been argued that one reason why oxidized Ga can be supercooled by as much as 35 K ($T_m=302.9$ K) is that the oxide coating removes nucleation sites for the crystalline gallium phase.[4] In addition, it is expected that the nucleation of an oxide layer on a liquid surface occurs differently than on crystalline surfaces, where oxides nucleate at step edges and other defects that do not exist on the atomically smooth liquid-metal surface. These expectations have been supported by recent secondary ion mass spectrometry (SIMS) measurements on liquid-gallium surfaces,[5–7] which have distinguished between oxide formation in an early-time or low-oxygen-dosage stage and a late-time or high-oxygen-dosage stage. In the early stage, oxides form spontaneously with a fractal-like structure[5–7] and in the latter stages, large oxide islands are readily observed.[7]

These observations, however, do not provide information about the structure of the oxide overlayer, for example, the oxide film thickness, interfacial roughness, and atomic structure. Owing to the difficulty in applying x-ray and neutron scattering to a liquid-metal surface, there has been little progress in understanding these basic issues despite their practical importance. Recent synchrotron x-ray studies have demonstrated that the vapor interfaces of liquid mercury[8,9] and liquid gallium[10,11] can be investigated in great detail using x-ray reflectivity, which yields information on the electron density profile normal to the surface, and grazing incidence scattering, a technique sensitive to the atomic structure within the surface plane. These studies indicated that the near-surface metal atoms are stratified normal to the surface in atomic layers with a sub-angstrom surface roughness[8,10] and possess liquidlike order parallel to the surface.[9,11]

Here we report an x-ray study of the oxidation of liquid-gallium surfaces. Ga is ideal for such studies since (i) it has a very low vapor pressure, (ii) its surface can be cleaned and kept oxide-free with standard UHV techniques, and (iii) it is highly reactive and readily oxidizes at room temperature even with a partial pressure of oxygen as low as 10^{-7} Torr. We have dosed the clean liquid-gallium surface with oxygen, studied the surface with x rays under UHV conditions, and then reversibly stripped the oxide using ion sputtering. The x-ray reflectivity measurements were carried out at the wiggler beam line X-25 at the National Synchrotron Light Source using a liquid reflectometer with a water-cooled Ge(220) crystal monochromator set to reflect at $\lambda=0.6532$ Å. Details of the sample preparation, surface cleaning, data collection, and data analysis have been presented elsewhere.[10,12] The surface was exposed to research-grade molecular oxygen through a bakeable UHV leak valve; the dosage was monitored by a residual gas analyzer and an ion gauge. The oxygen exposure is expressed in langmuirs (1 $\mathrm{L}=10^{-6}$ Torr s), which is the dosage that would form a

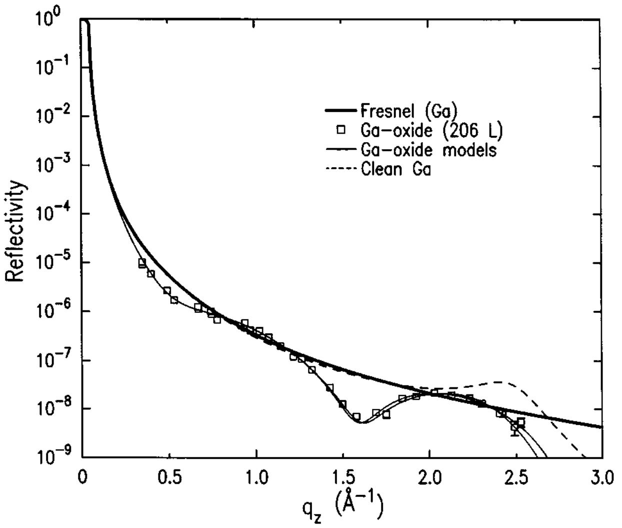

FIG. 1. Measured x-ray reflectivity vs wave vector q_z for the liquid-Ga surface exposed to 206 L of oxygen at room temperature (open squares) and for a bare liquid-Ga surface (dashed line) (Ref. 10). The Fresnel reflectivity R_f for an ideally abrupt and smooth surface is shown as a bold line. The two thin lines are fits to the models discussed in the text. The oscillations, observed for the oxidized surface but not for the bare one, are a clear indication of a well-defined surface oxide layer of a uniform thickness ~5 Å.

monolayer assuming a sticking coefficient of unity. For oxygen, 1 L=1×10^{-7} Torr for 24 s.[13] After the dosage procedure, the chamber was evacuated and the base pressure (on the order of 10^{-9} Torr) was recovered with an oxygen partial pressure on the order of 10^{-11} Torr.

For the clean gallium surface, the x-ray reflectivity, shown in Fig. 1 as the dashed curve, follows the Fresnel theory of reflectivity from an ideally flat surface out to wave-vector transfers $q_z\sim2$ Å^{-1}, with a quasi-Bragg peak at $q_z\sim2.4$ Å^{-1} due to surface-induced atomic layering.[10,12] Upon exposure to 206 L of oxygen, the reflectivity changes dramatically: the quasi-Bragg peak disappears and well-defined oscillations are observed. These oscillations, known as Kiessig fringes, are a clear indication of the formation of a surface oxide layer of uniform thickness. From the period of the fringes $\Delta q_z\sim1.2$ Å^{-1}, the thickness of the oxide can be estimated by $2\pi/\Delta q_z\sim5$ Å. This is consistent with the SIMS measurements, where it is speculated that the oxide film is no more than a few monolayers thick.[7]

The principal features in the data are highlighted by normalizing the measured reflectivity to the Fresnel reflectivity R_f of an ideally flat surface, as shown in Fig. 2, where a series of data recorded at different oxygen exposures is illustrated. The well-defined maximum in the R/R_f ratio at $q_z\sim2.4$ Å^{-1} prior to oxygen exposure is seen to diminish gradually with 80–180 L of oxygen and ultimately disappears. At the same time, two sets of maxima ($q_z\sim1.0$ and 2.2 Å^{-1}) and minima ($q_z\sim0.4$ and 1.5 Å^{-1}) start to develop with increasing oxygen dosage. Their fixed positions, from the lowest dosage measured and up, indicate that the oxide layer thickness is fixed. The increasing intensity difference between the minima and the maxima reflects the increasing coverage of the liquid surface by the oxide layer: for low dosages (80–150 L) the coverage is small, while for 206 L and above the coverage is almost full, as found also in the ion-microscopy studies.[7] Since the two maxima have approximately the same amplitude, neither the liquid metal/oxide nor the oxide/vacuum interface can be very rough, and on the basis of the quantitative analysis presented below, we will conclude that both interfaces must be atomically sharp. In addition, our data clearly show that the thickness and uniformity of the oxide film remains unchanged over the several mm^2 illuminated region in the center of the sample, even at high oxygen doses (1600 L). These observations are in contrast to the liquid-Ga surfaces studied by ion microscopy, where the perimeter of the oxide islands is found to be thicker or less uniform than their interior.[7]

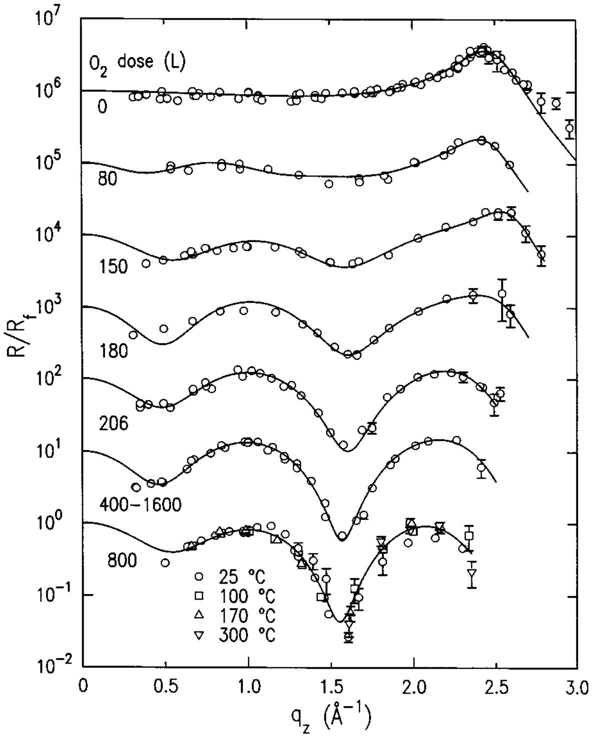

FIG. 2. Measured reflectivities, normalized to the Fresnel reflectivity, for liquid-Ga surfaces dosed with an increasing amount of oxygen (open symbols). The data are offset by factors of 10 for clarity. There is no discernible variation in the period of the R/R_f oscillations once the oxide adlayer has formed. At 800 L, the sample temperature was varied up to 573 K without observable changes in the reflectivity. The modified distorted crystal model discussed in the text was used to fit these data (solid lines).

More quantitative information can be obtained by numerical modeling of the reflectivity data. Within the Born approximation[14] the measured reflectivity $R(q_z)$ is related to the average electron density along the surface normal $\langle\rho(z)\rangle$ by

$$\frac{R(q_z)}{R_f\,(q_z)}\approx\left|\frac{1}{\rho_\infty}\int\frac{d\langle\rho(z)\rangle}{dz}\,e^{iq_z z}dz\right|^2 \tag{1}$$

with ρ_∞ the known bulk Ga electron density. Typically, the density profile is constructed from a physical model for $\langle\rho(z)\rangle$, inserted in Eq. (1), and fitted to the reflectivity to extract the surface parameters that best describe the data. The fact that the measurement is confined to a finite range of q_z

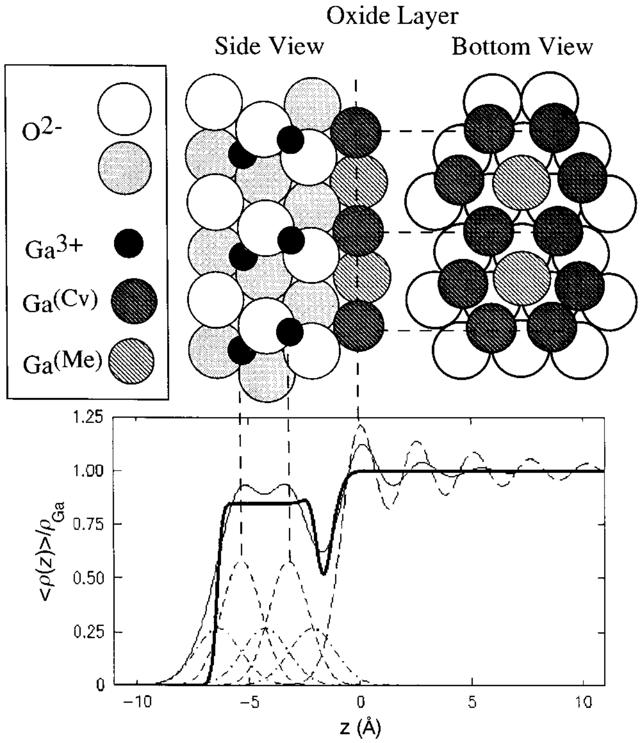

FIG. 3. Real-space models for the 206-L data shown in Fig. 1. Top: the proposed atomic arrangement in the oxide layer, with atomic diameters of 2.64 Å for O^{2-}, 1.24 Å for Ga^{3+}, 2.44 Å for covalent (Cv) Ga, and 2.50 Å for metal (Me) Ga. Bottom: the corresponding electron density profile (thin solid line) with its separate components; the underlying liquid Ga (large dash line) and the Gaussians representing the Ga^{3+} (dash-dotted line) and O^{2-} layers (short-dashed line). The oxide adlayer contains three planes of oxygen atoms with Ga^{3+} ions in locations suggested by the α- and β-Ga_2O_3 structures. The bold line is the simple box model discussed in the text.

together with the inherent inability to determine the phase of the reflected wave allows a certain degree of ambiguity in the density profile. Nevertheless, the relatively simple form of the observed $R(q_z)/R_f\ (q_z)$ suggests an electron density profile with two well-defined interfaces, leading to constructive and destructive interference of the reflected x rays and the consequential oscillatory features in the reflectivity. We begin with a simple model that is constructed from constant density slabs (box model) convoluted with a Gaussian function representing the roughness of the interfaces. The simple density model, shown as the bold line in Fig. 3, fits the reflectivity extremely well as demonstrated by the solid lines in Fig. 1. The key features of this model are that the liquid/oxide and oxide/vacuum interfaces are atomically flat: the fits yield a root-mean-square width of 0.72±0.2 Å at the liquid/oxide interface and 0.33±0.1 Å at the oxide/vacuum interface. The thickness of the oxide layer is 4.9±0.2 Å and the density relative to the Ga bulk density is 0.848±0.016. In addition, a density deficit at the liquid/oxide interface must be incorporated to fit the data, which represent an oxide-liquid transition layer.

Using the phenomenological model above as a starting point, we now proceed to construct a more fundamental, chemically motivated, atomic model for the oxide layer and its interface with the liquid. X-ray photoemission studies have shown that the oxide that forms on crystalline Ga surfaces is likely β-Ga_2O_3 or highly defective α-Ga_2O_3.[15] Thus, for this atomic model, we have constructed a picture that illustrates how Ga_2O_3 can be plausibly oriented with respect to the liquid-Ga surface. We assume that the liquid-metal surface is similar to the close-packed (001) face of α-Ga, which is the stable phase at STP and is a metal with pronounced covalent character. The Ga unit cell is orthorhombic and the structure can be visualized as a stacking of distorted close-packed layers. Each Ga atom is weakly bound to the neighboring six atoms in the layer and strongly bound to a single Ga atom in a plane either above or below it, leading to a description based on covalently bound Ga_2 dimers.[16] From an analysis of the bulk liquid structure factor,[17] similar covalent character has been argued to exist in the liquid, and more recently simulations[18] and extended x-ray-absorption fine-structure experiments[19] have shown that significant orientational correlations exist in liquid Ga. Given this, we propose that the topmost layer of the liquid-Ga surface contains a modest number of Ga ions, which covalently bond with the first layer of O^{2-} ions in the Ga_2O_3 structure. The oxide adlayer consists of alternating layers of Ga^{3+} and O^{2-} ions, with it terminated by an O^{2-} layer. This picture of the bonding is consistent with the photoemission results of Su *et al.*[15]

It is straightforward to incorporate this description of the interface into the distorted crystalline model developed for the liquid Hg (Ref. 8) and Ga surfaces.[10,12,20] In this model, the liquid metal is composed of equally spaced atomic layers, each represented by a Gaussian function, where the density distribution along the surface normal of each layer is broadened by mean square displacements (MSD's) that increase with distance into the bulk liquid. The Gaussians have an interlayer spacing denoted by d and the MSD of the jth layer ($j=0,1,2,\ldots$) follows a simple form $\sigma_j^2=\sigma_{\rm CW}^2+j\bar{\sigma}^2$, with $\sigma_{\rm CW}$ a common displacement to each atomic layer, due to surface capillary wave excitation,[20] and $\bar{\sigma}$ a measure of the increasing displacement of each layer as the bulk liquid is approached. This leads to an oscillatory profile near the liquid-metal surface, representing atomic layering, and a uniform density beneath it. In the model described here, the Ga ions that interface the liquid metal to the oxide are included with the density of the topmost metal layer; these Ga ions form tetrahedra with the first plane of close-packed O^{2-} ions (Fig. 3). The next layer is made up of Ga^{3+} ions, which lie in octrahedral sites, according to preferences in the local atomic bonding. The oxide film continues with additional layers of O^{2-} and Ga^{3+} ions.

The density profile for the modified distorted crystalline model that best describes the data at 206 L is shown as a thin solid line in Fig. 3, and there is good agreement between the data and the model (Fig. 1). Furthermore, the two model reflectivities provide nearly identical profiles. The density profile contains three planes of O^{2-} ions, two planes of Ga^{3+} ions, and a certain fraction of Ga ions in the topmost liquid layer to interface with the oxide. The parameters that describe the layering in the liquid Ga have been fitted to $\bar{\sigma}=0.59\pm0.02$ Å and $\sigma_{\rm CW}=0.95\pm0.01$ Å with the interlayer spacing fixed at $d=2.5$ Å. To maintain an overlayer with a stoichiometry of Ga_2O_3, the electron density (or integrated area) of an O^{2-} Gaussian was fixed at (10 e^-/at.)×(0.147 at./Å^2) and for a Ga^{3+} Gaussian at (28 e^-/at.)×(0.0982 at./Å^2), which are computed from the structure of β-Ga_2O_3.[21] The Ga^{3+} and O^{2-} Gaussians are equally spaced at 1.06 ±0.03 Å, consistent with the spacings in the α- and β-Ga_2O_3 structures, and the Gaussian widths are determined to be 0.88 ±0.04 Å for Ga^{3+} and 1.02±0.2 Å for O^{2-}. The best-fit distance between the oxide layer and the first Ga layer in the liquid metal is 2.15±0.06 Å; consistent with the diameter of the gallium and oxygen ions.

Fits to both density models indicate that the average overlayer density is lower than that for pure Ga. In contrast, the calculated electron densities for both β-Ga_2O_3 (1.64 e^-/Å^3) and α-Ga_2O_3 (1.80 e^-/Å^3) are similar to, or greater than, pure Ga (1.63 e^-/Å^3). This implies a partial coverage of the Ga surface by the oxide. If the oxide layer resides in patches over an underlying smooth gallium subphase and if the patches are smaller than the x-ray coherence area (see below), then the oxide coverage is calculated to be 85%. In fact, qualitatively this is what might have been expected from the imaging experiments,[7] which illustrate that even in the late-time or large-dosage stages of oxidation, corresponding to oxygen dosages similar to the largest studied here, only 88% of the surface is covered with oxide. These images indicate that fractal-like interfaces exist between oxide coated and clean regions, and if the same is true for our liquid-Ga surfaces, the model profile might be expected to be a coherent average of the two. For the modified distorted crystalline model, the coverage ratio is fit as an additional parameter, leading to 0.76±0.03, which indicates a fractional coverage of ~76% of Ga_2O_3 on the liquid surface.

In the foregoing discussion, the density profiles have been calculated and fit to the data assuming the amplitudes of the x rays reflected from the oxidized and bare Ga regions add coherently. That is, the amplitude of the scattered radiation from the oxidized and bare regions are added rather than their intensities. We have also analyzed the data assuming that the scattering adds incoherently from a bare liquid-Ga surface that is partially covered with a Ga_2O_3 adlayer. However, the low-q_z data ($q_z < 1.2$ Å^{-1}), which dips below the Fresnel reflectivity (Fig. 2), cannot be fit with the incoherent models, since the reflectivities at low q_z from either of the two surfaces alone are equal to or greater than R_f. Only if there is coherence between the oxidized and bare regions, leading to destructive interference in the scattering amplitude, is it possible to fit the low-q_z data. This implies that bare and oxidized regions are always present together on length scales comparable to the x-ray coherence length of 1000–3000 Å in these experiments, which is consistent with the diffusion-limited aggregation morphology observed in previous microscopy studies.[7] The images do show, however, some extended bare regions that are larger than the x-ray coherence length. Although the oxide coverage in our sample may be more uniform over these larger length scales, without additional information it is not possible to model that here.

The agreement obtained from the two fits demonstrates that the reflectivity can be modeled with or without atomic layering of the liquid metal near the liquid/oxide interface. However, it has been argued that the sharp liquid/vapor interface and the layering phenomenon observed in liquid metals have a common origin that, on a macroscopic level, is manifested by the exceptionally large surface tension.[8,10,20] The observation of a very sharp liquid/oxide interface suggests a similar situation, making the existence of atomic layering plausible here as well.

To complement the reflectivity experiments, grazing-incidence x-ray scattering (GIXS) measurements were undertaken on the fully formed gallium oxide layer, but no sharp in-plane peaks corresponding to an ordered oxide were observed. It is therefore likely that the oxide adlayer is amorphous, as is the native oxide Al_2O_3 on crystalline aluminum surfaces[22] or at least poorly crystallized. Although the only known gallium oxide glass (to our knowledge) is Ga_2O_3, which is a very poor glass former,[23] it is anticipated that it is considerably easier to form Ga_2O_3 as an amorphous film on a disordered substrate like a liquid metal. Since the liquid-gallium surface is curved, however, it is extremely difficult to perform GIXS measurements, i.e., to maintain the angle between the incident beam and the surface at or below the critical angle over the entire surface area illuminated by the beam. For a more definitive test of in-plane structural order of the oxide, this measurement should be repeated with flatter samples.

Reflectivity data were also obtained on an oxidized surface at temperatures up to 573 K. The surface was prepared by dosing with 800 L of oxygen at room temperature (bottom curve of Fig. 2). No changes in the reflectivity are recorded with increasing temperature. Hence, for these temperature changes, there is essentially no variation of the oxide layer thickness or density. More significantly, the surface roughness is also unchanged as the temperature is increased, which is in contrast to the large dependence observed for the bare liquid-Ga surface, where capillary waves increase the surface roughness by about 30% and consequently reduce the x-ray reflectivity by a factor of 2 at $q_z \approx 2.0$ Å^{-1} with only a modest change in temperature (from room temperature to 443 K).[20] This is a strong indication that the oxide layer is solid, suppressing thermal capillary waves that would otherwise exist on a liquid surface.

These results have provided a look at the atomic arrangements of an oxide overlayer on any liquid-metal surface. It is intriguing that some of the salient features found here, i.e., the oxide thickness saturation at only 5 Å and the amorphous in-plane structure, are also found for oxides formed on some polycrystalline solids, such as Al, in spite of the vastly different underlying surface morphology: an ultrasmooth liquid surface for Ga and a stepped, imperfect but crystalline surface for solids. Extension of these measurements to other liquid metals is clearly called for to allow a better understanding of what is the common behavior and what is metal specific in the industrially and scientifically important process of liquid-metal surface oxidation.

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[1] O. Kubaschewski and B. E. Hopkins, *Oxidation of Metals and Alloys* (Academic, New York, 1962).

[2] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon, New York, 1984), p. 243.

[3] T. Iida and R. I. L. Guthrie, *The Physical Properties of Liquid Metals* (Clarendon, Oxford, 1993), p. 109.

[4] M. Hida, A. Sakakibara, and H. Kamiyabu, J. Jpn. Inst. Metals **53**, 1263 (1989).

[5] Y. L. Wang, A. Raval, and R. Levi-Setti, Scanning Microsc. **3**, 731 (1989).

[6] Y. L. Wang and S. J. Lin, Phys. Rev. B **53**, 6152 (1996).

[7] J. M. Chabala, Phys. Rev. B **46**, 11 346 (1992).

[8] O. M. Magnussen, B. M. Ocko, M. J. Regan, K. Penanen, P. S. Pershan, and M. Deutsch, Phys. Rev. Lett. **74**, 4444 (1995).

[9] S. W. Barton, B. N. Thomas, F. Novak, P. M. Weber, J. Harris, P. Dolmer, J. M. Bloch, and S. A. Rice, Nature **321**, 685 (1986).

[10] M. J. Regan, E. H. Kawamoto, S. Lee, P. S. Pershan, N. Maskil, M. Deutsch, O. M. Magnussen, B. M. Ocko, and L. E. Berman, Phys. Rev. Lett. **75**, 2498 (1995).

[11] E. B. Flom, Z.-H. Cai, A. Acero, B.-H. Lin, N. Maskil, L. Liu, and S. A. Rice, J. Chem. Phys. **96**, 4743 (1992).

[12] M. J. Regan, P. S. Pershan, O. M. Magnussen, B. M. Ocko, M. Deutsch, and L. E. Berman (unpublished).

[13] A. Roth, *Vacuum Technology* (Elsevier, Amsterdam, 1990), p. 3.

[14] P. S. Pershan and J. Als-Nielsen, Phys. Rev. Lett. **52**, 759 (1984).

[15] C. Y. Su, P. R. Skeath, I. Lindau, and W. E. Spicer, Surf. Sci. **118**, 248 (1982).

[16] J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974), p. 236.

[17] P. Ascarelli, Phys. Rev. **143**, 36 (1966).

[18] X. S. Gong, G. L. Chiarotti, M. Parrinello, and E. Tosatti, Europhys. Lett. **21**, 469 (1993).

[19] A. DiCicco and A. Filipponi, Europhys. Lett. **27**, 407 (1994).

[20] M. J. Regan, P. S. Pershan, O. M. Magnussen, B. M. Ocko, M. Deutsch, and L. E. Berman, Phys. Rev. B **54**, 9730 (1996).

[21] S. Geller, J. Chem. Phys. **33**, 676 (1960).

[22] A. E. Evans (private communication).

[23] L. E. Topol, D. H. Hengstenberg, M. Blander, R. A. Happe, N. L. Richardson, and L. S. Nelson, J. Non-Cryst. Solids **12**, 377 (1973).