SURFACE SCIENCE LETTERS

REEXAMINATION OF THE InSb(111) AND GaSb(111) STRUCTURES: COMMENT ON 'DISORDER IN THE RECONSTRUCTED (111)2 × 2 SURFACES OF InSb AND GaSb' BY A. BELZNER, E. RITTER AND H. SCHULZ

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A recent article [Surface Sci. 209 (1989) 379] has attempted to improve the agreement between our original X-ray diffraction data [Phys. Rev. Letters 54 (1985) 1275; Surface Sci. 186 (1987) 499] and the proposed distorted vacancy model by the introduction of an additional, partially occupied atom in the unit cell. Here we show that almost as much improvement can be obtained by introducing second-layer displacements into the original structure. This raises questions of uniqueness in crystallographic structure determination and the level of detail attainable without overinterpretation of data.

The distorted vacancy model (fig. 1) for the InSb(111)2 × 2 and GaSb(111)-2 × 2 surfaces has been proposed to explain X-ray diffraction data measured with synchrotron radiation at HASYLAB [1,2]. The refined coordinates of the atoms revealed bonding geometries of s^2p^3 for surface Sb and sp^2 for surface In and Ga that were consistent with the notion of electron transfer from the metal to the Sb. This tends to neutralize the atoms in the surface, relative to those of the bulk, which are sp^3 and therefore charged.

The quality of agreement of the model with the diffraction data was assessed by means of a statistical χ_1^2

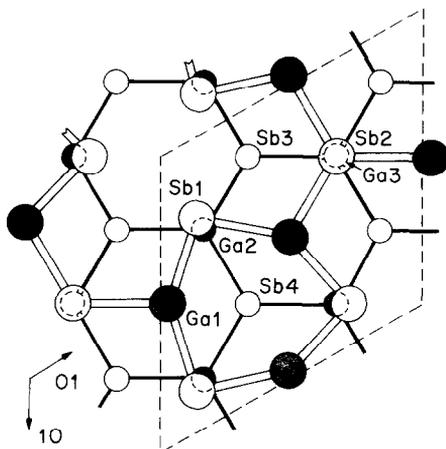$$\chi_1^2 = \frac{1}{N} \sum \frac{(F_o - F_c)^2}{\sigma_o^2}, \tag{1}$$

Fig. 1. The distorted vacancy model for GaSb(111)2×2. The unit cell is dashed. Open circles are Sb; shaded circles are Ga (or In). The second-layer atoms are smaller. The vacancy is a missing Ga that would lie at the unit cell origin in the unreconstructed surface.

where N is the number of observation, F_o is the observed value of the structure factor and F_c its value calculated from the model. σ_o is the (measured) experimental error of F_o. When the discrepancy in the fit is, on average, the same as the experimental error χ_1^2 will have value unity; larger values indicate systematic differences, while significantly lower values suggest that the data have been interpreted to a level of detail not justified by the experimental uncertainty. The published values of χ_1^2 were 1.8 for InSb [1] and 2.0 for GaSb [2].

The uniqueness of a model depends on the accuracy of the data. This was tested in the following ways. If an atom was omitted from or added to the model for InSb, even after optimization of coordinates, χ_1^2 was found to rise to more than 30 [1]. If the Ga and Sb atoms in GaSb were substituted by a single atom type, χ_1^2 went up to 17 [2]. In this way we were confident that we had the correct number and assignment of atoms. Nevertheless, as Belzner et al. have pointed out [3], a χ^2 of 2 still leaves some room for improvement. The improvement, however, must be more subtle than adding a whole atom; Belzner et al. achieve this by adding an atom with 10% occupancy [3]. In this comment, we argue that this is not the only possibility: we obtain comparable improvements with distortions in the *second layer*. Such second-layer distortions are allowed within the symmetry of the original model and we believe this to be the more physically realistic explanation.

For ease of comparison we have adopted the same definition of χ^2 used by Belzner et al. [3]

$$\chi_2^2 = \frac{1}{N - P} \sum \frac{(F_o - F_c)^2}{\sigma_o^2},$$ (2)

which includes the number of degrees of freedom in the fit, P. Statistically speaking, this is the more useful definition because it establishes whether the addition of an extra parameter to the model is significant or not [4]: χ_1^2 is always reduced when more degrees of freedom are permitted, but not necessarily χ_2^2. We continue to use $1/\sigma^2$ weighting in our least-squares refinement because this uses the data optimally and is statistically correct. It is true that unit weights give a greater selectivity between models but are prone to bias from the less reliable data. The results presented here have been tested with both weighting schemes and do not differ significantly between them.

The published structural models of InSb(111)2×2 [1] and GaSb(111)2×2 [2] gave χ_2^2 values of 3.8 and 4.2 respectively using the new definition of eq. (2) and a new computer program with more accurate evaluation of the low-angle form factors. The R-factors were 0.073 and 0.078 where R is the usual crystallographic reliability factor:

$$R = \sum (\mid F_o \mid - \mid F_c \mid)/\sum \mid F_o \mid. \tag{3}$$

We then confirmed the defect structures published by Belzner et al. [3] indeed gave improved fits. For InSb(111), an additional In site at (0.9475, -0.9475) with occupancy 0.078 gave an extremely good fit with $\chi_2^2 = 0.42$ and $R = 0.025$, in an 8 parameter fit. For GaSb(111), an additional Ga at (0, 0) with occupancy 0.14 gave improvement but less drastically so, ending with $\chi_2^2 = 3.7$ and $R = 0.068$ in a 5 parameter fit. The In site did not work for GaSb(111) as Belzner et al. also found [3].

At a surface, the translational symmetry of the bulk is broken in the perpendicular direction. The continuous symmetry means that layers of structure are no longer identical and displacements of atoms from their bulk positions exist in principle to any depth into the crystal. This would be true for both the original vacancy model as well as the defect structure proposed by Belzner et al. Therefore we investigated the effects of second-layer displacements in the original model for which we refer to fig. 1. In the figure, Sb1 and Ga1 move radially away from and towards the 3-fold axis passing through Sb4, as in the original model. In the second layer Ga2 and Sb3 are allowed to move along their mirror symmetry lines while Ga3 and Sb4 are constrained on 3-fold axes. For InSb(111) both displacements were found to be significant as were individual temperature factors for In1, Sb1 and Sb2. We obtained $\chi_2^2 = 1.48$, $R = 0.040$ with 8 parameters. For GaSb(111) the individual B factors were not statistically significant. The result here was $\chi_2^2 = 1.38$, $R = 0.047$ with 6 parameters. This best fit is shown in fig. 2. Both sets of refined structural parameters are given in table 1.

Examination of the parameters in table 1, allows us to make some specific remarks about the surface structure. A caveat, repeated below, is that this is not a unique model: the defect model of Betner et al. [3] is also a good description, at least for InSb(111). We wish to argue, though, that the
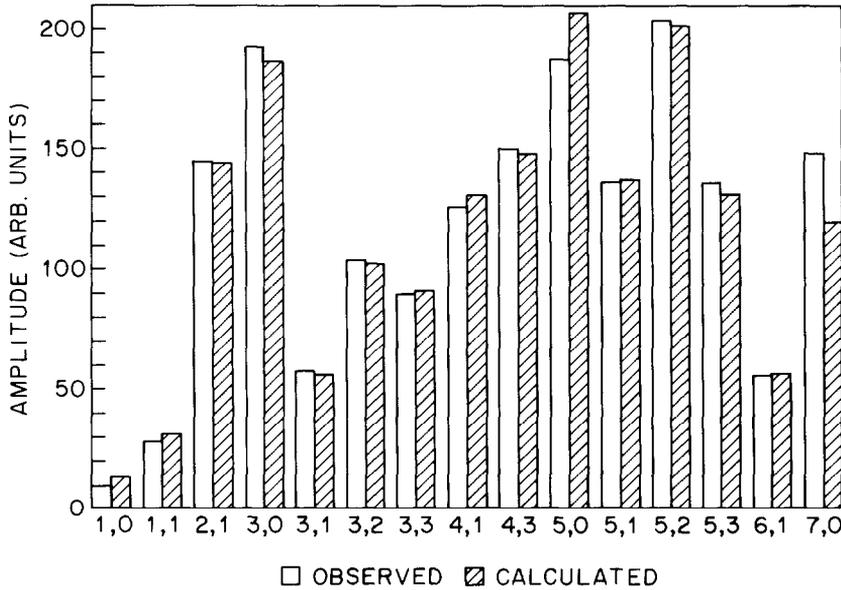
Fig. 2. Observed and calculated structure factor amplitudes for the best fit to GaSb(111)2×2. The 2D Miller indices of the reflections (×2 for brevity) are written under the bars. This fit has
$$\chi_2^2 = 1.38.$$

description of second-layer displacements is physically reasonable and not exotic. The second-layer atom with the larger displacement is In2/Ga2 which lies directly below Sb1 and is bonded to it. The relative displacement ratio (second layer/first layer) of $15 \pm 2\%$ for InSb and $12 \pm 3\%$ for GaSb is a small value compared with other surfaces: 25% for W(001)$\sqrt{2} \times \sqrt{2}$ [5] and 44% for Sn/Ge(111)$\sqrt{3} \times \sqrt{3}$ [6]. This displacement is reasonable in magnitude and

Table 1
Refined atomic parameters for the new model containing second-layer displacements

Atom	InSb(111) $\chi^2 = 1.48$			GaSb(111) $\chi^2 = 1.38$		
	x	y	B (Å^2)	x	y	B (Å^2)
In/Ga1	0.5141 (7)	0.028	0.9 (9)	0.5131 (6)	0.026	
Sb1	0.280 (1)	0.140	2 (2)	0.2849 (6)	0.142	0 (2)
Sb2	0.333	0.667	1 (1)	0.333	0.667	
In/Ga2	0.3240 (9)	0.162		0.328 (1)	0.164	
In/Ga3	0.333	0.667	1.5	0.333	0.667	1.5
Sb3	0.1674 (4)	0.335		0.1643 (4)	0.329	
Sb4	0.667	0.333		0.667	0.333	

Atom labels refer to fig. 1. The (x, y) coordinates are given crystallographically, as fractions of the unit cell along the 10 and 01 directions (see fig. 1).

expected for symmetry reasons, since the bonds surrounding In2/Ga2 are no longer exactly tetrahedral on account of the involvement of the displaced Sb1. The individual temperature factors are in order $B_{Sb1} > B_{In1} > B_{Sb2}$ which is the same order as their connectivity starting with the most loosely bound atom Sb1.

The defect model of Belzner et al. [3] for InSb has a χ_2^2 of 0.42, which implies that the average discrepancy between the model calculation and the data is *substantially less* than the errors in the data themselves. This apparent statistical "fluke" is less surprising when one considers the number of possible ways an "atom" of adjustable height could be fit into a difference map. Improvements which also make chemical sense are harder to find by the difference method and sometimes impossible, as in the case of a small displacement. Our description not only is intuitively realistic, but works for *both* InSb(111) and GaSb(111). The small excess χ_2^2 above unity leaves room for the effects of deeper displacements, anisotropic thermal motion or even a small number of defects in the structure, but we do not believe there is any more that can be said reliably without a big improvement in the data.

Second layer displacements also affect the fits to out-of-plane "rod scan" data that were published for GaSb(111) [2]. The size of the displacement proposed here, however, is so small that the change is within the error bars of the data.

In summary, we have shown that the residual information in the X-ray data for the InSb(111)2 × 2 and GaSb(111)2 × 2 surfaces can be explained simply by permitting the distortions of the distorted vacancy model to extend down to the second layer. The small second-layer displacements encountered in both surfaces are realistic in that they are largest for In/Ga2, which is bonded directly underneath Sb1 (with the largest displacements in the surface layer). Both displacements are in the same direction. It is important to state, however, that there is no way to distinguish this model from the disorder model of Belzner et al. from the crystallographic data alone.

Generally speaking, surfaces will have more means available to them to disorder because they have lower symmetry than 3D crystals. But the continuous symmetry in the perpendicular direction also means that a large number of small distortions is to be expected, greatly adding to the structural degrees of freedom. Both effects are subtle and only seen in the crystallographic analysis once the basic structure, at the level of the total number of atoms, has been elucidated. The lesson to be learned is that crystallographic data, as with any other kind, must not be overinterpreted. A χ^2 of 2 certainly means that more information can be gleaned, but does not offer much of a constraint on the possible refinements of models. Here we find at least two totally different ways of accounting for the residual; while the model of Belzner et al. introduces a new physical concept and new binding geometries, our model includes second-layer distortions that are bound to be present anyway.

References

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