

STRUCTURAL DETERMINATION OF THE InSb(110) SURFACE BY THE AUTOMATED TENSOR LEED PROGRAM

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The InSb(110) surface structure has been re-examined using the tensor LEED approach. A refinement of the structure as well as the influence of the Debye temperature on the structure determination is presented.

1. Introduction

As the LEED analysis employs a trial-and-error approach, a complete solution of complex surfaces with a large number of structural and nonstructural parameters is unreliable. Usually, structural parameters are more deeply investigated whereas little work has been carried out on the determination of nonstructural variables that are used as input to the LEED calculations. This approach has been justified by the observation that nonstructural parameters have smaller influence on the $I(V)$ curves than those related to the atomic positions. In fact, once one has good values for the structural parameters of the surface it is possible to use the LEED analysis to estimate nonstructural parameters. This is particularly useful in the case of the Debye temperature. It is well known that the measured LEED intensities depend on temperature. As the temperature is increased the LEED spots become weak and the background intensity is enhanced. The standard procedure to take into account the temperature effects is to use complex scattering phase shifts. Within this approach, only harmonic, isotropic and uncorrelated vibrations are considered. Although this procedure is a simplification which probably does not hold for the outmost surface atoms, one can obtain effective values for the Debye temperature that may represent an average of the first layers of atomic

vibrations, and it has been applied very successfully to a number of structural analyses.^{1–4} As the methods for measuring vibration amplitudes at surfaces are rare, their determination from LEED analysis becomes very important.

Among the computer programs used in the LEED analysis, the recently developed “Automated Tensor LEED Program” (ATLP)⁵ offers the advantages of performing an investigation of a nonstructural parameter whereas an automatic optimization of the structural parameters can be performed. This program allows a search in a large volume in the parameter space than the others. As the structural study of complex surfaces, such as those of III–V compound semiconductors, requires several parameters to be varied, the ATLP seems to be a useful approach to a more detailed surface structure determination. In this paper we present the results of a re-examination of the atomic structure of the InSb(110) surface by using the ATLP where the Debye temperature (Θ_D) of the surface is investigated in more detail.

2. Experimental Data and Theoretical Aspects

The experimental data used in this work was collected using a computer-controlled LEED diffractometer built at York, and the experimental setup and data collection have been described elsewhere.^{6,7}

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The theoretical analysis was performed assuming the muffin tin model for the crystal, with a muffin tin radius of 1.4026 Å for both atoms. The atomic wave function⁸ for each atom was used on the scattering potential calculation and a Slater parameter α of 2/3 was assumed for the local exchange approximation. Since the $I(V)$ curve calculation depends on the phase shifts, these were evaluated by numerical integration of the radial part of the Schrödinger equation within the muffin tin spheres.

The LEED calculation was performed in a Sun SPARC station SLC and the ATLTP code was used to evaluate the $I(V)$ curves. A set of nine phase shifts and a sample temperature of 293 K were assumed. The lattice vibration effects were accounted for using a set of complex phase shifts.⁹ Initially, the inner potential was assumed to be equal to $V_0 = -(10 + 4i)$ eV, but the real part of this potential (V_{0r}) was optimized in the analysis. The algorithm used for the minimization section was the Direction-set Search.¹⁰

Since the ATLTP code does not allow inclusion of the Debye temperature among the parameters to be automatically optimized, in order to start with the structural parameter optimization, we have used a fixed value for $\Theta_D = 160$ K and those structural parameters found by de Carvalho *et al.*⁶ The optimization was performed using the r-factor proposed by Pendry¹¹ as the function to be minimized. As we have no *a priori* reason for assuming that the final structure represents a global rather than a local minimum, the search procedure was started from several different positions within parameter space. When the minimization process was completed, we assumed the best structure found as the new reference structure and then we repeated all the procedure. After four iterations we found what we believe to be the best structure for the InSb(110) surface characterized by a first layer bond rotation of $\omega \approx 32^\circ$ at a fixed Θ_D .

In order to investigate the possible existence of the two minima in the r-factor analysis,⁶ we executed the ATLTP code in a region corresponding to a small bond rotation angle ($\omega \approx 4^\circ$) using the previous value of Θ_D . In this step a “bulk structure” was used as the starting point to the program. After two iterations we have obtained the best structure corresponding to this minimum.

After this initial structural survey at a fixed Θ_D , we proceeded with the refinement of the structure by varying the Debye temperature. The ATLTP was run using, as an input, different values of Θ_D (from 100 K to 1000 K). We started the search with the parameters defined by the best fit in the first optimization, i.e. the structure characterized by $\omega \approx 32^\circ$. In this step we used two r-factors: the one proposed by Pendry and the X-ray factor (R_1) as defined in Ref. 13. For each Θ_D a minimization for both r-factors, as a function of the structural parameters and V_{0r} , was performed. In order to achieve this we started the search, for each Debye temperature, at about 20 distinct points in the parameter space, with a maximum displacement of 0.3 Å away from the reference structure. As, for each starting point, the ATLTP minimization process searches about 500 different structures in order to get a minimum in the r-factor, the total number of structures examined for each Θ_D is about 10^4 .

3. Results and Discussion

Firstly, in order to test the ATLTP package, we ran the program using, as an input, the same set of structural parameters that were obtained with the CAVLEED program.⁶ The structure resulting from the ATLTP was very similar to that obtained from the CAVLEED, giving $R_P = 0.38$ and $R_1 = 0.39$. From this result we could believe that the ATLTP was working properly. The results from the search using, as a starting point, the parameters defining a “bulk structure” and $\Theta_D = 160$ K showed that there is a minimum in the R_P analysis at a bond rotation angle of about 3° with $R_P = 0.60$. In this case, the minimum is not as deep as that observed at a structure characterized by a high bond rotation angle ($\omega \approx 32^\circ$), here $R_P = 0.38$.

Thereafter, an intensive investigation of the effect of the Debye temperature on the InSb(110) surface structure optimization was carried out. The behavior of the r-factors, as a function of Θ_D , is shown in Fig. 1. From this figure one can see that the Pendry r-factor (R_P) is nearly constant from about $\Theta_D = 120$ K up to 1000 K, with a very shallow minimum ($R_P = 0.38$) observed at about $\Theta_D = 190$ K. On the other hand, the X-ray r-factor exhibits a well-defined minimum ($R_1 = 0.37$) at about 180 K. As the r-factor analysis shows clearly, the

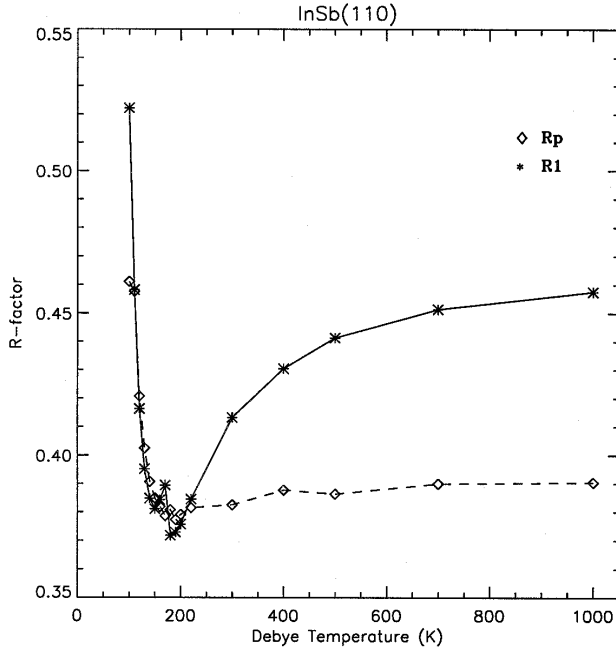


Fig. 1. The behavior of the R-factors used in the optimization as a function of the Debye temperature Θ_D .

determination of the structure is not straightforward. If the minimum in R_1 is chosen as an indication of the best structure, one can see that each r-factor, at the same Θ_D , provides structures that agree with each other only qualitatively. As is shown in Table I, in the structure resulting from an R_1 analysis there is no first layer relaxation — defined as $\frac{1}{2}(|\Delta x^{\text{Sb}}| - |\Delta x^{\text{In}}|)$ — and the atomic lateral displacements (parallel to the symmetry axis) show a bond length expansion of 0.29 Å, whereas in the structure obtained from R_P analysis the relaxation amounts to 8% of the interlayer spacing and there is a bond length contraction of 0.20 Å. There are also differences in the second layer for atomic positions: using R_1 both anions and cations move upwards and with R_P the anion moves downwards and the cation moves upwards in the opposite direction. In the latter the atomic lateral displacements are very small compared to those resulting from R_1 analysis. In Table II the final structures of the InSb(110) surface for two

Table I. R-factor final structures for the InSb(110) surface at $\Theta_D = 180$ K obtained in this work and the structures reported in Refs. 6 and 12. The atoms displacements are defined from the bulk positions as shown in Fig. 2.

	R_P	R_1	Ref. 6	Ref. 12
	Final structure	Final structure		
First layer				
$\Delta x^{\text{Sb}}(\text{\AA})$	$\uparrow (0.23 \pm 0.05)$	$\uparrow (0.42 \pm 0.07)$	$\uparrow (0.20 \pm 0.03)$	$\uparrow 0.18$
$\Delta x^{\text{In}}(\text{\AA})$	$\downarrow (0.59 \pm 0.07)$	$\downarrow (0.50 \pm 0.09)$	$\downarrow (0.61 \pm 0.03)$	$\downarrow 0.60$
$\Delta y^{\text{Sb}}(\text{\AA})$	(-0.34 ± 0.15)	(-0.51 ± 0.13)	-0.32	-0.38
$\Delta y^{\text{In}}(\text{\AA})$	(-0.54 ± 0.16)	(-0.22 ± 0.15)	-0.63	-0.58
$\omega_1(\text{deg.})$	(30 ± 4)	(26 ± 4)	(32 ± 3)	28.8
Rumple (Å)	(0.82 ± 0.12)	(0.92 ± 0.16)	0.81	0.78
Relaxation (Å)	(0.18 ± 0.06)	(0.04 ± 0.08)	0.21	0.34
$\Theta_D(\text{K})$	(180 ± 50)	180	160	Rigid lattice
Second layer				
$\Delta x^{\text{Sb}}(\text{\AA})$	$\downarrow (0.01 \pm 0.05)$	$\uparrow (0.10 \pm 0.07)$	—	—
$\Delta x_2^{\text{In}}(\text{\AA})$	$\uparrow (0.14 \pm 0.08)$	$\uparrow (0.21 \pm 0.09)$	—	—
$\Delta y_2^{\text{Sb}}(\text{\AA})$	(0.05 ± 0.14)	(0.16 ± 0.13)	—	—
$\Delta y_2^{\text{In}}(\text{\AA})$	(0.08 ± 0.19)	(0.17 ± 0.15)	—	—
$\omega_2(\text{deg.})$	(5 ± 5)	(4 ± 5)	—	—
Rumple (Å)	(0.15 ± 0.13)	(0.11 ± 0.16)	(0.18 ± 0.06)	0.18
Relaxation (Å)	(-0.08 ± 0.06)	(-0.15 ± 0.08)	—	—
R-factor	(0.38 ± 0.06)	(0.37 ± 0.05)	$R_P = (0.49 \pm 0.04)$	—

Table II. R-factor final structures for the InSb(110) surface at $\Theta_D = 100$ K and $\Theta_D = 700$ K. The atom displacements are defined from the bulk positions as shown in Fig. 2.

	$\Theta_D = 100$ K R_P	$\Theta_D = 100$ K R_1	$\Theta_D = 700$ K R_P	$\Theta_D = 700$ K R_1
First layer				
$\Delta x_1^{\text{Sb}}(\text{\AA})$	$\uparrow 0.21$	$\uparrow 0.34$	$\uparrow 0.22$	$\uparrow 0.63$
$\Delta x_1^{\text{In}}(\text{\AA})$	$\downarrow 0.63$	$\downarrow 0.54$	$\downarrow 0.58$	$\downarrow 0.43$
$\Delta y_1^{\text{Sb}}(\text{\AA})$	-0.42	-0.52	-0.32	-0.35
$\Delta y_1^{\text{In}}(\text{\AA})$	-0.54	-0.37	-0.53	-0.20
$\omega_1(\text{deg.})$	29	26	30	31
Rumple (\AA)	0.85	0.88	0.81	1.07
Relaxation (\AA)	0.21	0.09	0.18	-0.10
Second layer				
$\Delta x_2^{\text{Sb}}(\text{\AA})$	$\downarrow 0.01$	$\uparrow 0.16$	$\downarrow 0.02$	$\uparrow 0.23$
$\Delta x_2^{\text{In}}(\text{\AA})$	$\uparrow 0.14$	$\uparrow 0.25$	$\uparrow 0.13$	$\uparrow 0.31$
$\Delta y_2^{\text{Sb}}(\text{\AA})$	0.07	0.04	0.04	0.29
$\Delta y_2^{\text{In}}(\text{\AA})$	0.16	0.10	0.11	0.32
$\omega_2(\text{deg.})$	5	3	5	3
Rumple (\AA)	0.15	0.09	0.16	0.08
Relaxation (\AA)	-0.06	-0.04	-0.06	-0.04
R-factor	0.46	0.52	0.39	0.45

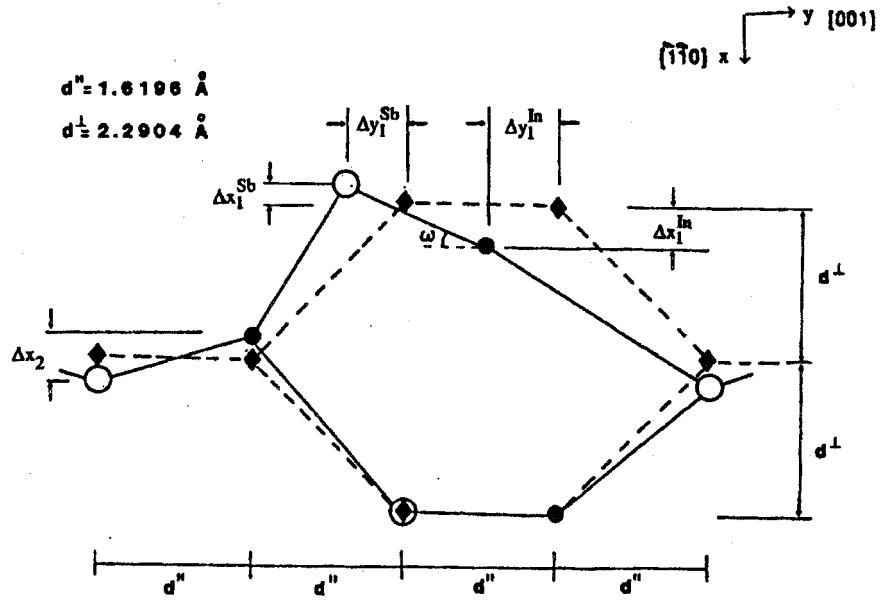


Fig. 2. Side view of the InSb(110) surface showing a model for top and second layer reconstruction. (●) In atoms; (○) Sb atoms; (◆) bulk atom sites.

representative values of Θ_D are also represented at points away from the value that gave the deepest minimum in the R_1 analysis. As we can see, by comparing the data from Tables I and II, the analysis based on R_P shows nearly the same structure for all the values of Θ_D . On the other hand, the R_1 analysis shows structures quantitatively different, mainly for high values of Θ_D . Therefore, as is clear from Fig. 1, from the analysis based on R_P it is difficult to precise what would be the best structure for the InSb(110) surface, since the observed minimum is very shallow. However, the X-ray r-factor (R_1) shows a well-defined minimum at about the same Θ_D but with a structure slightly different. Then, based on this analysis, R_1 shows more sensitivity to the variation of Θ_D than the R_P .

The behavior of the r-factors presented in Fig. 1 may be explained as follows: the Debye temperature is a nonstructural parameter which enters in the LEED intensity calculation through the Debye-Waller factor. This factor is then multiplied by the atomic amplitudes when one takes into account the lattice vibrations.¹⁴ In this way, this nonstructural parameter has great influence on the diffracted beam intensity but has little influence on the peak position which is presented on the $I(V)$ curves. Since the peak positions do not change very much when we vary Θ_D , we can expect the behavior showed by the R_P -factor. As the R_1 -factor is more sensitive to the peak intensities, this factor is able to de-

tect changes that appear on the intensities when we vary the Debye temperature. Then, the R_1 -factor seems to be more sensitive to Θ_D than R_P . A similar behavior for both r-factors was obtained by Riaño *et al.*¹⁵ for the CdTe(110) surface where the CAVLEED package was used for the LEED calculations.

We must point out that the data we have used were collected at room temperature and in that case the spectra are dominated by diffuse scattering at incident energies above about 140 eV. This corresponds to a narrow energy window for the analysis. Therefore, we may expect that a data set collected at lower temperature would improve the R_P sensitivity to the variation of Θ_D because more peaks will be present in the $I(V)$ curves.

In order to examine if there is a minimum in the r-factor analysis at a low bond rotation angle at $\Theta_D = 180$ K, we carried out a search using as a starting point to the ATLP, the parameters defining the "bulk structure." In fact both r-factors showed minima ($R_P = 0.58$ and $R_1 = 0.46$) at a rotation angle of about 2° that are not as deep as those observed at a structure characterized by a high bond rotation angle ($26^\circ < \omega < 30^\circ$).

The experimental $I(V)$ curves used in this work together with the theoretical $I(V)$ curves obtained by the ATLP for $\Theta_D = 180$ K are showed in Figs. 3 and 4. It must be observed that by visually comparing the curves in these figures it is not possible to

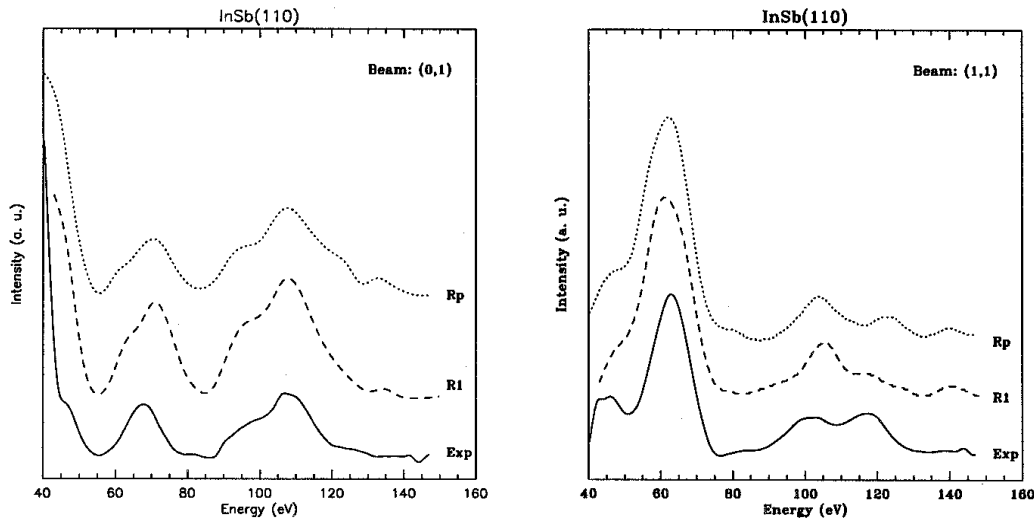


Fig. 3. InSb(110) experimental and calculated $I(V)$ curves for the structures presented in Table I.

distinguish what set of curves is in better agreement with the experimental data.

In Table I we also present the results from two other works on InSb(110). The study of Ref. 12 has been carried out by Meyer *et al.* using a data set collected at a temperature $T \approx 150$ K and intensities calculated for a rigid lattice, using a multiple scattering theory for the first three layers and a modified kinematical approach for deeper layers. Their conclusion was a surface bond length conserving rotation model, characterized by $\omega \approx 28.8^\circ$, and a second layer rumple of 0.18 \AA for the best fit to the experimental data. In Ref. 6 the same surface was investigated by de Carvalho *et al.* using a data set obtained at room temperature (RT) where a fully dynamical LEED calculation was carried out using the CAVLEED program described by Titterton and Kinniburgh.¹⁹ In this work, using the r-factor algorithm for theory-experiment comparison, it was found that a rotation model characterized by $\omega \approx 32^\circ$ and a second layer rumple of 0.18 \AA gives the best fit to the experimental data although a less deep minimum in the r-factor analysis was also observed at a rotation angle of $\omega \approx 4^\circ$. In the latter, the structural parameters have been intensively investigated whereas the nonstructural parameters have been varied only roughly.

Although from our r-factor analysis of the InSb(110) surface it is not clear which r-factor gives the best structure, we must emphasize that our results are in fact different from those reported in Refs. 6 and 12 — as can be seen in Table I — and they represent an improvement with respect to the previous works on that surface. Firstly, we have obtained a lower reliability factor ($R_P = 0.38 \pm 0.06$) with respect to that obtained in Ref. 6 ($R_P = 0.49 \pm 0.04$). Secondly, a much greater number of structures were investigated — about 10^4 structures for each Debye temperature. In the work of Ref. 16, an X-ray r-factor of 0.21 is reported. This value cannot be compared with our result for R_1 , because they used the relative quadratic deviation between experimental and computed intensities (R_2).¹³

The value of 180 K for the Debye temperature indicated by the minimum R_1 shown in Fig. 1 does not agree with what should be expected for the vibrational behavior of the surface atoms. For top layers of clean and unreconstructed solids a reduced surface Debye temperature is often used to describe enhanced vibrations of surface atoms with sufficient accuracy. In the case of the InSb the reported bulk Debye temperature is 144 K.⁷ Our result is about 25% higher than the bulk value and represents only

an effective value of Θ_D for the first surface layers. This means that the lattice at the surface is, on average, more rigid than that in the bulk. If that is the case, it must come from the reconstruction process undergone by the first surface layers as observed in almost all the III-V compound semiconductors.

4. Conclusion

From the results presented in this work we can firstly conclude that the ATLP reproduced nearly the same structure as the CAVLEED package. Secondly, the refined structure obtained for the InSb(110) surface is more representative, since a much larger region of the parameter space was investigated including an optimization of the Debye temperature. In addition, it is clear from this work that, at least for the data set we have examined, the X-ray r-factor (R_1) is more sensitive to the variation of the Debye temperature than the R_P . The best-fit structure obtained by R_1 is slightly different than that indicated by R_P , although both r-factors show minima with different depth at about the same $\Theta_D = 180$ K. This effective value of Θ_D is about 25% higher than the bulk value ($\Theta_D = 144$ K).¹⁷ This means that the surface layer lattice is, on average, more rigid than that of the bulk. However, it must be pointed out that the influence of the Debye temperature in the final structure of such systems has to be investigated in a more effective way, perhaps involving a layer-by-layer variation of this nonstructural parameter. This may be achieved by using, for example, the recently developed thermal tensor LEED approach.¹⁸

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