Accurate structure determination for GaAs using *Pendellösung* oscillation

M. Möhle, J. Stahn and U. Pietsch

Institute of Solid State Physics, University of Potsdam,
D-14415 Potsdam, Germany

Abstract

The sets of X-ray structure amplitudes for GaAs published by Matsushita and Hayashi[1] and by Pietsch[2] are completed by highly precise data recorded between $0.50\,\text{Å}^{-1} < \frac{\sin\Theta}{\lambda} < 1.35\,\text{Å}^{-1}$. For the strong reflections the required accuracy of $\Delta F/F \leq 1\%$ was realized by the use of *Pendellösung* measurements. At $\lambda = 0.30$ Å the integral intensities were recorded as a function of the effective thickness from a 500 μm thick GaAs wafer. Additionally, several weak reflections were determined from the integral intensities within the kinematic limit at at $\lambda = 0.56$ Å and 0.71 Å. Both experiments required synchrotron radiation. From our data we determined the individual temperature factors for gallium and arsenic and applied them for the calculation of the valence charge density map.

1 Introduction

The most characteristic feature of the valence charge density of GaAs is a charge density maximum between next neighbours slightly shifted towards the arsenic atom. This is explained by the overlap of bonding orbitals and the charge transfer between nearest neighbours. As shown recently,[3] only a few of the charge density maps calculated from different data sets of X-ray structure amplitudes, F_H, published till now, are in qualitative agreement with this theoretical prediction. A smooth density map is only obtained using the data of Matsushita and Hayashi [1] completed by the weak reflections measured by Pietsch [2].

Unfortunately, a separation of the influence of atomic thermal vibrations and bond charge is difficult, because the F_H are only available up to $\frac{\sin\Theta}{\lambda} < 0.64\,\text{Å}^{-1}$. Therefore additional data for higher $\frac{\sin\Theta}{\lambda}$ had to be recorded. The required accuracy of $\Delta F/F \leq 1\%$ can only be realized performing scattering experiments satisfying unambinguously either the dynamical or the kinematic theory.

Because of the proximity of gallium to arsenic in the periodic table the zincblende structure crystal GaAs exhibits Bragg reflections of very different scattering power. For small $\frac{\sin\Theta}{\lambda}$ the F_H of the class $h+k+l = 4n$ and $4n\pm1$ are about 100. Then the extinction length rules the integral intensites. Using conventional techniques of structure analysis they are strongly affected by secondary extinction which prevents the determination of precise F_H. To overcome this problem dynamical X-ray experiments have been realized like *Pendellösung*[4] and dynamical half-widths measurements [1]. On the other hand the class $h+k+l = 4n+2$ Bragg reflections are weak ($F_H < 10$). Their integral intensities are controlled solely by the absorption length. This justifies the use of conventional techniques taking care that the *Umweganregung* can be ruled out.

In this work we present *Pendellösung* measurements for strong F_H and conventional ones for weak F_H in order to complete the up to now best data by high order reflections. From our data we determined the individual temperature factors for gallium and arsenic (section 3) and applied them for the calculation of the valence charge density map (4).

2 Experiment

Our experiments were performed at the four-circle diffractometer of the D3 beamline at HASYLAB. Using a Si(111) double-crystal-monochromator the energy resolution of the incident beam was better than $\Delta E/E = 10^{-4}$. *Pendellösung* measurements were performed for several reflections between $0.50\,\text{Å}^{-1} < \frac{\sin\Theta}{\lambda} < 1.01\,\text{Å}^{-1}$ using GaAs plates with a thickness of about 500 μm oriented along [110] and [100], respectively. Using the

[1] T. Matsushita, J. Hayashi, *phys. stat. sol.* (*a*) **41**, 139 (1977).
[2] U. Pietsch, *phys.stat.sol.* (*b*) **103**, 93 (1981).
[3] U. Pietsch, N. K. Hansen, *Acta Cryst.* B, (1996) submitted.
[4] K. Kobayshi, T. Takama, S. Sato, *Jap. Jour. Appl. Phys.* **27**, 1377 (1988).

Table 1: Real and imaginary parts of F'_H and F''_H evaluated by *Pendellösung* and their comparison with F_0 calculated from the spherical model and using the temperature factor given in section 3.

hkl	$\frac{\sin\Theta}{\lambda}$	F'_H	F''_H	F'_0	F''_0
4 4 0	0.500	112.55	3.22	112.12	2.57
6 2 0	0.559	97.45	3.17	98.15	2.47
4 4 4	0.613	86.33	2.65	86.61	2.38
5 5 3	0.679	52.57	1.78	52.53	1.61
8 0 0	0.708	68.81	2.85	69.39	2.21
6 6 0	0.751	62.62	2.50	62.69	2.12
6 6 4	0.830	51.99	2.16	51.92	1.96
8 8 0	1.010	35.64	2.08	35.40	1.62

symmetrical Laue-case we recorded the integral intensities as a function of the effective thickness rotating the wafer by discrete angular steps Φ around the normal of the reflecting lattice plane. The wavelength $\lambda = 0.3\,\text{Å}$ was chosen in order to reduce absorption. The temperature was $297 \pm 1\,\text{K}$. The spot size on the sample was about $1\,\text{mm}^2$. According to Kato[5] the integral intensity R for the symmetric case oscillates like

$$R = \frac{\pi}{2} \left| \frac{F_H}{F_{\bar{H}}} \right| e^{\frac{-\mu t}{\cos\Theta\ \cos\Phi}} \cdot |B| \int_{-1}^{1} \left| J_0\left(B\sqrt{1-x^2}\right) \right|^2 \mathrm{d}x \tag{1}$$

with

$$B = \frac{r_e}{V} \frac{t\lambda\sqrt{F_H F_{\bar{H}}}}{\cos\Theta\ \cos\Phi} \tag{2}$$

in which R depends on the product $\lambda \cdot F_H \cdot t$. The *Pendellösung* of several reflections are shown in fig. 1 recorded between $-60° < \Phi < +60°$. The oscillation behaviour appeared only on sample areas which were free of dislocations. Owing to the epd $\leq 500\,\text{cm}^{-2}$ the number of useable reflections was limited. The evaluated F_H are shown in table 1 obtained via least square fit of eqn. (1) at the curves shown in fig. 1. The thickness t was determined using a contact method with an accuracy of about 0.2 %.

Additionally, F_H of several weak reflections were determined between $0.25\,\text{Å}^{-1} < \frac{\sin\Theta}{\lambda} < 1.35\,\text{Å}^{-1}$ collecting the integral intensities in Bragg-case geometry. Performing Ψ-scans around the normal of the reflecting lattice

[5] N. Kato, *J. Appl. Phys.* **39**, 2225 (1968).

Figure 1: Several curves displaying *Pendellösung*. For clarity they are vertically shifted.

hkl	$\frac{\sin\Theta}{\lambda}$	$s \cdot F_{\mathrm{meas}}$	$s \cdot F_{\mathrm{ext}}$	F_H	F_0
2 2 2	0.306	62.7	63.9	5.32	5.54
$\bar{2}$ 2 2	0.306	70.7	72.0	6.00	5.54
4 2 0	0.395	75.3	77.1	6.41	6.40
4 4 2	0.531	80.4	83.2	6.91	6.87
6 0 0	0.531	81.1	82.5	6.85	6.87
6 2 2	0.586	79.4	81.4	6.75	6.69
6 4 0	0.638	74.5	76.2	6.31	6.38
6 4 4	0.729	66.4	67.7	5.58	5.61
8 2 0	0.729	66.4	67.7	5.58	5.61
6 6 2	0.771	61.0	62.0	5.10	5.22
8 4 2	0.810	58.0	58.9	4.83	4.85
8 6 0	0.884	50.6	51.2	4.17	4.20
8 6 4	0.952	44.5	45.0	3.72	3.64
10 4 0	0.952	44.7	45.2	3.73	3.66
8 8 2	1.016	40.1	40.5	3.34	3.25
10 6 2	1.046	37.9	38.2	3.16	3.06
8 8 6	1.132	33.2	33.5	2.77	2.65
10 8 0	1.132	33.0	33.3	2.75	2.63
10 6 6	1.160	31.9	32.1	2.66	2.54
10 8 4	1.186	31.0	31.2	2.58	2.46
10 10 2	1.263	27.9	28.1	2.32	2.20
10 10 6	1.358	25.1	25.2	2.09	1.96

Table 2: Measured weak reflections at $\lambda = 0.56\,\text{Å}$, being proportional to $s \cdot F_{\mathrm{meas}}$, after extinction correction $s \cdot F_{\mathrm{ext}}$ and after scaling and correction for dispersion F_H and their comparison with F_0 (spherical model) using the temperature factors highlighted in section 3. s is a scale factor.

plane we found several angular regions which were free from *Umweganregung*. The measurements were made at two different wavelengths, namely $\lambda = 0.56\,\text{Å}$ and $0.71\,\text{Å}$. Due to absorption the crystal thickness could be treated as semi-infinite. In order to check the validity of the kinematic theory the measured intensities were corrected for secondary extinction (see column 2 in table 2). The maximum correction did not exceed 2%. Except of 222 and $\bar{2}22$ the F_H which are corrected by dispersion and evaluated F_H are very close to the values calculated from the spherical model (see section 3). Generally, the accuracy of our data is higher than published up to now.[6] [7] [8]

3 Determination of temperature factors

There is some disagreement among the individual temperature factors published till now. Our data are accurate enough to verify these values. We used only F_H with $\frac{\sin\Theta}{\lambda} > 0.5\,\text{Å}^{-1}$ so that bonding effects do not have to be considered. Two different fitting procedures were applied. First, we made a fit via

$$F_H = 4\left[f_{\mathrm{Ga}} e^{-B_{\mathrm{Ga}}\left(\frac{\sin\Theta}{\lambda}\right)^2} \pm f_{\mathrm{As}} e^{-B_{\mathrm{As}}\left(\frac{\sin\Theta}{\lambda}\right)^2}\right] \tag{3}$$

using the free atomic scattering factors f_{Ga} and f_{As} from the *International Tables*[9]. For weak reflections F_{w} (negative sign in eqn. (3)) this yields the linear dependence $B_{\mathrm{Ga}} = 1.2 \cdot B_{\mathrm{As}} - 0.007$. Fitting the values for the seven strong reflections given in table 1, F_{s} (plus sign), we obtain $B_{\mathrm{Ga}} = -1.2 \cdot B_{\mathrm{As}} + 1.34$. Both lines cross at a point corresponding to $\boldsymbol{B_{\mathrm{Ga}} = 0.667\,\text{Å}^2}$ and $\boldsymbol{B_{\mathrm{As}} = 0.561\,\text{Å}^2}$ (293 K).

A second procedure consists in plotting $-\ln(F_{\mathrm{s}} + F_{\mathrm{w}})/8f_{\mathrm{As}}$ and $-\ln(F_{\mathrm{s}} - F_{\mathrm{w}})/8f_{\mathrm{Ga}}$ against $(\frac{\sin\Theta}{\lambda})^2$ which follows simply from eqn. 3. The slopes of both Wilson plots give $B_{\mathrm{Ga}} = 0.653\,\text{Å}^2$ and $B_{\mathrm{As}} = 0.549\,\text{Å}^2$ (293 K). They are about 2% smaller compared with the results of the first procedure. Our temperature factors are slightly smaller compared with those published by Levalois & Allais [6] but they verify our formerly applied values [3].

[6] M. Levalois, G. Allais, *Acta Cryst.* B **42**, 442 (1986);
[7] R. Saravanan, S. K. Mohanlal, K. S. Chandrasekaran, *Acta Cryst.* A **48**, 4 (1992);
[8] A. W. Stevenson, *Acta Cryst.* A **50**, 621 (1994).
[9] *International Tables for Crystallography* Vol.C, (1995) A. J. C. Wilson, Editor; Kluwer Academic Publishers, Dordrecht.

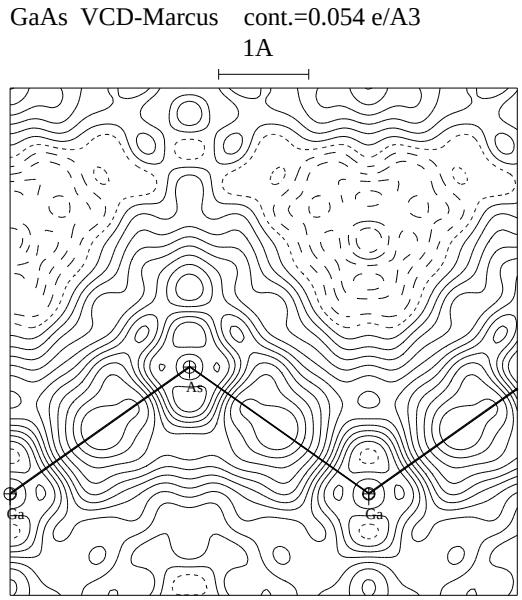

Figure 2: Valence charge density map calculated by use of our data and those given by [1] and [2]. The contour lines are spaced by $0.054\,\mathrm{e/\AA^3}$.

4 Calculation of the valence charge density and discussion

The data published by Matsushita *et al.* [1] and Pietsch [2] were completed by the values presented in tables 1 and 2. Now, the data set contains 16 strong/medium and 17 weak reflections having an individual accuracy better than 1%. We corrected the F_H by dispersion using a procedure described in [3] and applying the highlighted B_{Ga} and B_{As} given above. The valence charge density map was calculated via Fourier summation of structure factor differences

$$\Delta F = F_H e^{-i\chi} - F_{\mathrm{core}} e^{-i\sigma} \tag{4}$$

The F_H are the experimental data, the F_{core} are calculated ones using the core scattering factors published in [9]. The scattering phases σ are obtained using the model of spherical atoms whereas χ was obtained applying a bond charge model given in [2]. In practice, σ and χ differ only for 111, 222, and 442. The calculated map is shown in fig. 2. The density maximum is slightly shifted towards the arsenic atom and the bond charge is shaped asymmetrical. This is in agreement with theoretical predictions based on pseudopotential and density functional calculations. Our density maximum of $0.67\,\mathrm{e/\AA^3}$ is in fairly good agreement with that given by Chelikowsky & Cohen ($0.70\,\mathrm{e/\AA^3}$)[10]. A detailed comparison between experimental and theoretical density maps reveals several discrepancies. These concern the negative contours close to $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ in our map and regions close to the atomic sites.

However, the comparison of experimental and theoretical F_H displays additional disagreements. To realize that the theoretical data calculated by using the LAPW-DF method[11] were multiplied by an overall Debye-Waller factor, which differ for strong/medium and weak reflections (see the procedure given section 3). Especially for small $\frac{\sin\Theta}{\lambda}$ the theoretical data are closer to the spherical model than to the experimental values. This discrepancy has to be understud by further theoretic studies.

5 Acknowledgements

The authors thank K. Eichhorn and H.-G. Krane (HASYLAB) for experimental assistence, P. Blaha (Wien) for supplying the theoretical F_H and N. K. Hansen (Nancy) for drawing the density map. This work was supported by the BMBF (grant 05 647IPA) and the European Community (grant CHRX-CT93-0155).

[10] J. C. Chelikowski, M. L. Cohen, *Phys. Rev.* B **14**, 556 (1976).
[11] P. Blaha, K. Schwarz, P. I. Sorantin, S. B. Trickey, *Comput. Phys. Commun.* **59**, 399 (1990).

References

[1] T. Matsushita, J. Hayashi, *phys. stat. sol.* (*a*) **41**, 139 (1977).

[2] U. Pietsch, *phys.stat.sol.* (*b*) **103**, 93 (1981).

[3] U. Pietsch, N. K. Hansen, *Acta Cryst.* B, (1996) submitted.

[4] K. Kobayshi, T. Takama, S. Sato, *Jap. Jour. Appl. Phys.* **27**, 1377 (1988).

[5] N. Kato, *J. Appl. Phys.* **39**, 2225 (1968).

[6] M. Levalois, G. Allais, *Acta Cryst.* B **42**, 442 (1986).

[7] R. Saravanan, S. K. Mohanlal, K. S. Chandrasekaran, *Acta Cryst.* A **48**, 4 (1992).

[8] A. W. Stevenson, *Acta Cryst.* A **50**, 621 (1994).

[9] *International Tables for Crystallography* Vol.C, (1995) A. J. C. Wilson, Editor, Dordrecht: Kluwer Academic Publishers.

[10] J. C. Chelikowski, M. L. Cohen, *Phys. Rev.* B **14**, 556 (1976).

[11] P. Blaha, K. Schwarz, P. I. Sorantin, S. B. Trickey, *Comput. Phys. Commun.* **59**, 399 (1990).