Dynamical scattering of X-rays by real binary crystals and problem of point defects

L.I.Datsenko*, V.P.Klad`ko *, V.F.Machulin *, S.Manninen $, I.V.Prokopenko*

*Institute of Semiconductor Physics NASU , Kiev, Ukraine
$Department of Physics , Helsinki University , Helsinki, Finland

Abstract. One of the important subjects in the material science of semiconductor compounds is a problem of stoichiometry. The methods based on the measurement of kinematical integral reflectivity (IR) , R_i^K , for the quasi-forbidden reflection (QFR) of X-rays were formerly used for investigation of the $GaAs$ composition. To determine the value of deviation from stoichiometry, $\Delta = c_A - c_B$ where c_i is a concentration of the component A or B, one should make some corrections for extinction phenomena which is difficult to take into account for a real (with defects) crystal. The reflectivity of a real crystal for a QFR, R_i^D , may be also described within the dynamical theory taking into account the Debye-Waller static factor , L_H , the extinction coefficient μ_{ds} , and parameter Δ . To determine these characteristics the experimental thickness pendulum oscillation of $R_i^D(t)$ (200 reflection, λ=0.1198nm) was measured and analysed for the first time . By this the Hönl corrections of atomic formfactors for anomalous dispersion were made. Another independent approach consisted in analysis of the experimental energetic dependence of the $R_i(\lambda)$ for the wavelengths situated between the two absorption K-edges was used too . Relatively close values of the L_H and μ_{ds} for GaAs crystals with dislocations as well as parameter Δ were obtained by fitting of the $R_i^D(t)$ and $R_i^D(\lambda)$ nonlinear functions, calculated by the theory , to the experimental data.

INTRODUCTION

Nonstoichiometry and point-like defects is one of the most important problems in the material science of binary crystals which are widely used today in solid state devices technology [1]. It is well known that these defects are usually investigated by means of various optical and electrophysical methods [2]. Results obtained by these methods are needed to be proved by other independent investigations, for example, by the x-ray diffractometrical ones . But they, unfortunately have very low sensitivity to points defects even in the case when such dynamical phenomena as Borrmann effect are used [3]. Diffuse scattering of X-rays is sensitive to defect clustering only [4]. So for an enhancement of X-ray of X-ray scattering one use sometimes laborious methods [5]. Nevertheless utilisation of reflectivities of so called quasiforbidden reflection permits to study nonstoichiometrical distortions of a binary crystal sublattice [6].Such approach supposes utilization kinematical case of diffraction where the total reflectivity does not depend on structure perfection of a crystal. More realistic

CP514, *Theory and Computation for Synchrotron Radiation Spectroscopy,*
edited by M. Benfatto, C. R. Natoli, and E. Pace

situation is however the case of dynamical scattering when a real defect structure should be taken into account [7].

The aim of this paper was to obtain the quantitative independent information not about nonstoichiometry of a GaAs crystal only but the values of integral characteristics of crystal perfection i.e. the Debye-Waller static factor L_H and coefficient of extinction due to diffuse scattering on defects μ_d too. For this purpose the measurements of the Pendellösung intensity oscillations for the QFRs and so called energetical or wavelength dependent reflectivities were carried out. These experiments were made for the wavelengths of X-ray continuous spectrum situated close to the absorption K-edges of the As and Ga components where the Hönl corrections for atomic formfactors due to anomalous dispersion are essential what is of principle for developed experimental methods.

THEORETICAL BASES OF EXPERIMENTAL METHOD

Thickness oscillations of reflectivities for the QFR`s

Pendellösung fringes in a differential reflectivity R as it is well known may be described for a perfect crystal by the following formula accounting contribution of the both Bloch`s waves with a weak and strong absorption as well as oscillation term :

$$R = 0.25 \cdot \left\{ \exp\left[-\frac{\mu t}{\cos\vartheta}(1-\varepsilon) \right] + \exp\left[-\frac{\mu t}{\cos\vartheta}(1+\varepsilon) \right] - 2\exp\left[-\frac{\mu t}{\cos\vartheta} \right] \cos(2\alpha) \right\} \quad (1)$$

were $\alpha = \pi \left| \chi_{rh} \right| ct / (\cos\vartheta \cdot \lambda)$ is the ratio of thickness t and extinction length Λ.Here μ, ε, χ_{rh}, C stand for coefficient of absorption, parameter of a wave field localization in a crystalline lattice, real part of the Fourier coefficient of susceptibility and polarisation factor. χ_{rh} as well as imaginary part of the mentioned Fourier coefficient χ_{ih} depend on the corresponding part of structure factor F_h :

$$\chi_{rh} = r_a \left(\frac{\lambda^2}{\pi V} \right) F_{rh}$$

$$\chi_{ih} = r_a \left(\frac{\lambda^2}{\pi V} \right) F_{ih} \quad (2)$$

where r_a , λ and V are respectively the classical electron radius ; wave– length of radiation and a volume of an elementary lattice . For a QFR the F_h value is proportional to the difference of atom form factors of components :

$$F_H = 4\ (F_{GA} C_{GA} 2057\ \ - F_{AS} C_{AS}) \qquad (3)$$

where C_{Ga} and C_{As} are the concentrations of components in corresponding sublattices . By measurements using the wavelengths situated near the absorption K-edges the Hönl corrections for the real Δf ` and imaginary Δf `` part of scattering should be taken into account :

$$f = f_0 + \Delta f' + i\Delta f'' \qquad (4)$$

When some disorder there is in one of sublattices, let in the A , the parameter nonstoichiometry $\Delta = C_A - C_B$ may be introduced. So the QFR`s are perspective for determination of the Δ parameter which is determined by a little variation of a component concentration. For the case of substitution of native atoms by the others ones (let it be the silicon atoms with concentrations $C_{S\,i}$) the structure factor of such crystal may be written in the following way :

$$F_h = \left\{(1 - C_{Si})\left[(f_0 + \Delta f')_{As} + \Delta f''_{As}\right] + C_{Si}(f_0 + \Delta f')_{Si} - C_{Ga}\left[(f_0 + \Delta f')_{Ga} + \Delta f''_{Ga}\right]\right\} \quad (5)$$

So when measuring the Pendellösung fringes distance for the QFRs one may determine the parameter Δ contrary the case of an usual structural reflection where it can not be done . But practically this procedure is difficult to realize because the extinction distance Λ for the QFRs is very large due to little value of the corresponding structure factor F_h (3) . This obstacle can be met using the wavelengths situated near the Ga absorption K-edge [7]. In this case the Hönl corrections Δf_{Ga} may considerably change the value of F_h . All the said relates to the case of a perfect crystal. For a real crystal with structure defects the integral reflectivity R_i for the QFRs depends on the Debye-Waller factor L_H and the coefficient of additional energy losses parameter μ_{ds} due to diffuse scattering on defects (extinction) . In this case the formulas of the Molodkin dynamical theory [8] should be used taking into account the Bragg, R_B , and diffuse , R_D, components of total reflectivity R_i :

$$R_i = R_B + R_D \ . \qquad (6)$$

Using the mentioned formulas and the known fitting procedure for the measured thickness dependencies of a total reflectivity, R_i^{exp}, one can determine not only the structure perfection characteristics L_H and μ_d of a real crystal but the nonstoichiometry parameter Δ too [7].

Energetical dependence of the R_i for the wavelengths situated between the Ga and As absorption K-edges.

Utilization of the continuous spectra of X-rays gives another (independent) possibility for determination of the mentioned three parameters. In this region of wavelengths a special point exists where the real part of a structure factor and therefore the corresponding value of χ_h go to zero due to effect of the Hönl correction

[9,10].. In this case we were trying to apply again the Molodkin`s theory developed for the Bragg case of diffraction [11,12]. So both of the components R_B and R_D of a total reflectivity R_i in (6) now depend on the L_H and μ_d parameters :

$$R_B(\Delta\vartheta) = \xi(L - \sqrt{L^2 - 1}) \qquad (7a)$$

$$R_D(\Delta\vartheta) = F_{din}(\Delta\vartheta)\frac{\mu_d(k_0)\gamma_0}{2\mu_i(\Delta\vartheta)}. \qquad (7b)$$

Meanings of the diffraction parameters ξ and L are denoted in [13] . The values F_{dyn} $(\Delta\theta)$, $\mu_i(\Delta\theta)$, $\mu_d(k_0)$ were discussed in [14]. One should note by this that the coherent component of scattering (7a) depends on the Hönl correction of the corresponding atom form factors F_{Ga} and F_{As} for anomalous scattering near the absorption K-edges (4). It permits to calculate the reflectivity of a crystal near the mentioned specific point where the F_{rh} and $\chi_{rh} \rightarrow 0$.

PECULIARITIES OF THE EXPERIMENTAL TECHNIQUES

The thicknes Pendellösung fringes were observed by us for the first time for 200 reflections of a *GaAs* crystal using the wavelength λ=*1.1965*Å situated close to the *Ga* absorption K-edge (λ_{KGa}=1,1957Å) in the longwave region[7]. Supply regime of the X-ray unit (U= 20 kV,I = 30 mA) permitted us to get rid of multiple harmonics of continuous spectrum. Very thin (t~100μm) samples were used to get an intensity level to be in excess of the background .They were step-like tilted in the angular interval α= ±60° around the diffraction vector direction. The normalized values of reflectivity *r :*

$$r = \overline{R}_i / R_i^K \cdot 2A + 1 - I_0(\mu t\varepsilon) \qquad (8)$$

were used to exclude an influence of photoelectric absorption. Here R_i and R_{iK} are respectively the measured value and calculated one for the kinematical case of diffraction. $A = \pi t/\Lambda$. $I_0(\mu\varepsilon t)$ is the Bessel function of zero order. For the wavelength λ= 1,1965Å the extinction length Λ_{200} is equal to 0,0053cm, where as for the 400 reflection this value is equal to 0,0016cm. To illustrate the difference of Λ values between the QFR 222 and the usual reflection 111 the calculations according formula (1) were carried out for a GaP crystal (Fig.1). One can see the larger Pendelösung distance for 222 reflection even in the case of a GaP where a difference $f_{Ga} - f_{As}$ is not so little as in GaAs sample. So utilization of the longwave region near the Ga absorption K-edges is justified The similar methods were used for measurements of the energetical dependences of reflectivities for the wavelengths in the interval between λ_{KGa} and λ_{Kas} excepting only the tilt of a sample. By calculation of reflectivities close to the point where the imaginary part of F_h ,*i.e.* F_{ih} exits only this

last value was taken into account. The parameters of structure perfection i.e. L_H, μ_d and Δ have been determined by the fitting procedure of the calculated value $R_i^T(\lambda)$ to the experimental ones $R_i^{exp}(\lambda)$. The minimum of the functional:

$$\Phi = \sum_{i=1}^{n} \left[R_i^{\exp}(\lambda)_i - R_i^T(\lambda)_i \right]^2 / \sigma_i^2 \qquad (9)$$

was looking for. The number of iterations was chosen in such a way that the accuracy of calculation was not worse 2÷3 % .

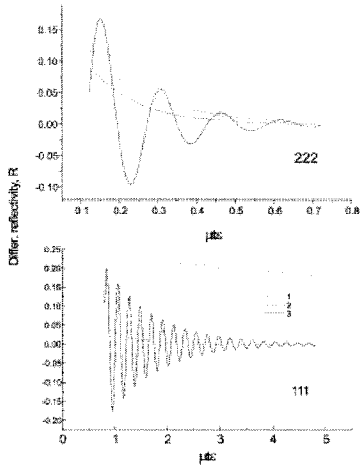

Fig.1. Calculation of the Pendellösung phenomenon for the 222 QFR and "usual" 111 reflection for a GaP perfect crystal (formula 1). Dashed and dotted lines correspond to the Bloch waves with low and strong absorption of X-ray (λ= 1.1984 **Å**

Results and their discussions

The thickness dependence of the normalized reflectivity of the 200 QFR r to a kinematical value R_i^K is shown in the (Fig 2) for the *GaAs* crystal containing some dislocation (density $N_d=8\bullet10^4 cm^{-2}$). One can see difference between the real nonstoichiometrical sample (the curve 2) and for a perfect stoichiometric crystal (curve 1). The fitted calculated curve is shown by the solid line in the upper part of the graph. One can see also that the upper graph (measured and calculated) are considerably displaced relatively lower curve 1 due to effect of diffuse scattering parameter μ_d. The curve 2 changes also the maxima and minima coordinates . It is an effect of structure defects (dislocations) via parameter of L_H. The last effect depends also on the level of nonstoichiometry because the best fit (the solid line 2 in the upper graph) can be reached in the case only when the parameter Δ is taken into account.

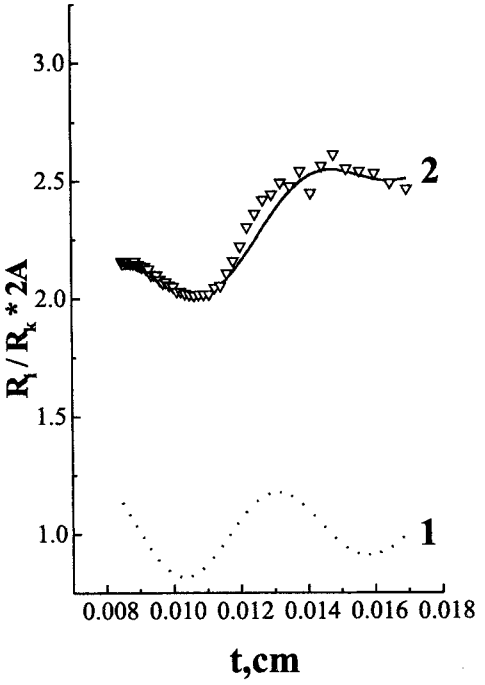

Fig.2. Thickness dependences of a reflectivity for the GaAs crystal containing $8 \cdot 10^4 cm^{-2}$ dislocations (curve 2) and for a perfect stoichiometric sample (calculation) (curve 1). λ= 1.1984 Å. The experimental results are shown by points.

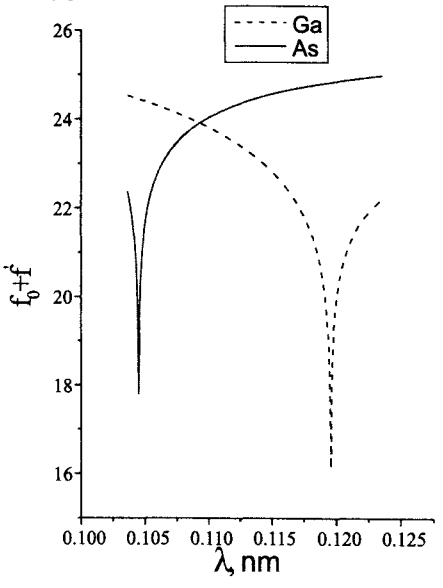

Fig.3. Variations of the Ga and As formfactors with changing of wavelengths between λ_{KGa} and λ_{KAs}.

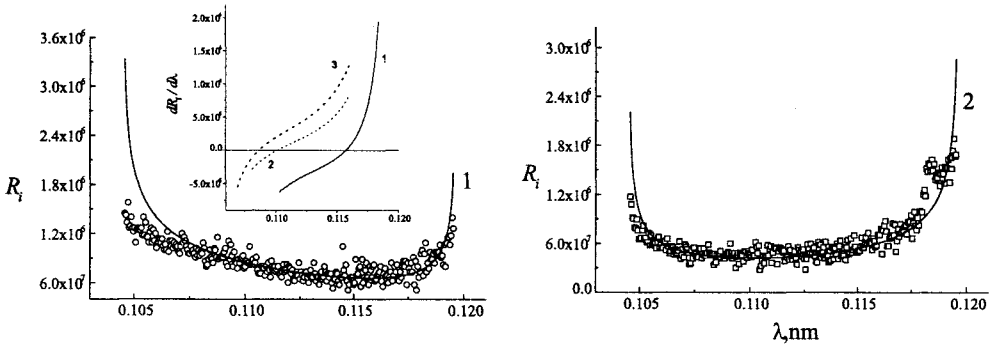

Fig.4. The energetical dependences of a reflectivity for GaAs crystals dopped with Si .C_{Si} are equal 1

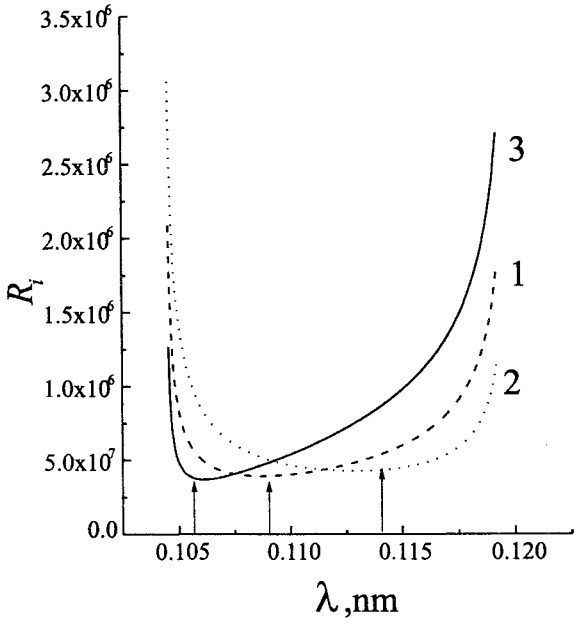

Fig.5. Effect of Ga(2) or As(3) excess on the reflectivity minimum close to the point where $F_{rh} \to 0$. The stoichiometrical sample is shown by curve 1.

Let us proceed to the results of investigations of the energetical dependences of R_i. First of all we consider the character of gallium and arsenic atom formfactors variations (Fig.3.) One can see that there is an equality of $(f_0 + \Delta f')_{Ga}$ and $(f_0 + \Delta f')_{As}$ values for the one specific wave length where $F_{rh} \to 0$. The exact positions of such points which are directly connected with a level of nonstoichiometry of a crystal can be determined by the known procedure of an extremum searching. Behaviour of the $dR_i/d\lambda$ function is shown in the insert to the Fig.4 for the fitted curves 1 and 2 for the samples with different concentration of Si atoms in GaAs crystals.

Effect of the Ga and As excess on the position of R_i minimum (pointers) is shown in the calculated curves 2 and 3 relatively the the stoichiometric sample (Fig.5.). So when analyzing the shape of the $R_i(\lambda)$ energetical dependences one can judge about the excess of one or other component even on a qualitative level. The carried out investigations have shown that structure defects do not influence the position of the discussed point. Really crystal imperfections can only displace the corresponding curves along the y axis.

Let us now compare the results of the L_H , μ_d ,and Δ parameters determination by two discussed methods (Table 1). It is ease to see that all of these parameters are relatively close. This correlation can be considered as satisfactory taking into account that it is difficult to measure the same point on the surface of a sample.

rdrrMethod	L_H	μ_d,cm^{-1}	Δ
Pendellösung fringes	0.052 ± 0.004	31 ± 3	0.00030
Energetical dependences of R_i	0.067 ± 0.003	18 ± 3	0.00032

Table 1. Integral characteristics of structure perfection , L_H , μ_d ,and parameter of nonstoichiometry for GaAs crystal as determined by the two independent methods for the 200 qusiforbidden reflection

CONCLUSIONS

Possibility of the integral characteristics of structure perfection (L_H , μ_d) and nonstoichiometry parameter Δ determination by the two independent experimental methods based on the integral reflectivity measurements for a quasiforbidden reflection of X-ray continuous spectrum was shown. Contrary to the known methods used the kinematical approximation of scattering, utilization of the dynamical phenomena (Pendellösung fringes or energetical dependencies of a reflectivity for the wavelengths situated between the absorption K-edges of binary crystal components) permits to study real binary crystals containing various structure defects. The developed methods is supposed to take into account the anomalous scattering phenomena near the K-edges of absorption of lattice components. The method of energetical dependence of reflectivity was developed for the Bragg case of diffraction what gives the unique possibility to study nondestructively the thin crystal film structures. This method uses the nonlinear character of energetical dependence of reflectivity with the special point were the imaginary part of structure factor exists only. Both of the methods assume utilization of the fitting procedure of calculated dependences by the Molodkin dynamical theory to experimental results and could be applied to experiments with synchrotron radiation.

REFERENCES

1. Bardsley W./ J.Cryst.Growth.-1980.-48. .-p.505
2. Lannoo M.,Bourgodin J. *Point defects in Semiconductors*. Berlin, Springer Verlang 1981, 263
3. Iveronova V.I., Katsnelson A.A., Kisin V.I., *Fizika Tvrdogo Tela* **11**, 3154 (1969).
4. Krivoglaz M.A. *Theory of x-ray and thermal neutron scattering by real crystals* 1969 New York; Plenum press p.192
5. Haubold H.-R, *G.Appl Cryst* **175** (1975)
6. Fujimoto I. Gap. *G. Appl Phys* **23** n5.-L287. (1984)
7. Datsenko L.J., KladkoV.P.,Melnyk V.M., Machulin V.F., *Metal physic and advanced technology* (in Russian). – 1999 .- - p.
8. Datsenko L.Y., MolodkinV.B., Osinovski M.E., *Dynamical scattering of x-rays by real crystals*. (In Russian) Naukova dumka . 1988, p196.
9. Kato N./Acta Cryst .-1992 .- A48 ,-p.829
10. Fukamashi T. ,Kawamura T. , *Acta cryst* **A49** 38 (1993)
11. Gavrilova E.N. , Kislovski E.N. , Molodkin V.B., Olikchovski S.I., *Metallofizyka* **3**- p 70 (1992)
12. Bar`yakhtar V.G., Gavrilova E.N., Molodkin V.B., Olikhovskii S.I., *Metallofizyka*. **14** n3 68 (1992)
13. Pinsker Z.G. *X-ray crystal optic* , M: Nauka, 390 (1982) (in Russian)
14.V.B.Molodkin, V.V.Nemoshkalenko, S.I. Olikhovskii, E.N.Kislovski, O.V.Reshetnyk, T.P. Vladomirova, V.P. Krivitsky , V.F. Machulin, I.V. Prokopenko, G.E.Ice, B.C.Larson, *Theoretical and experimental principles differential –integral triple-crystal x-ray diffractometry of imperfect single crystals* / preprint UNSC (Ukrainian national syncrotron centre) 3 1998, Kyiv 1998.p.23