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INTERACTION OF RADIATIONS WITH SOLIDS

Diffraction of X-Rays with Different Wavelengths for Quasi-Forbidden Reflections and Testing of the Nonstoichiometry in Binary Single Crystals

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The influence of structure defects and deviation from nonstoichiometry on X-ray scattering was studied over a wide wavelength range using quasi-forbidden reflections. It was found that equations of the kinematic theory of scattering can be used to analyse integral intensity. The possibilities and drawbacks of existing methods of the monocrystals nonstoichiometry control are analysed. A new method of such a control based on the analysis of intensities near *K*-edges of absorption for crystal components is proposed.

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1. INTRODUCTION

The structural defects occurring during the process of the growth of ingots cause degradation phenomena and decrease ingot-to-devices yield. In this connection the problem of development and improvement of research techniques of structural perfection of binary crystals, especially nondestructive methods, is of particular interest. First of all, there are X-ray diffractometry methods which, unlike topographical methods, allow us to reveal quite small distortions such as impurity and vacancy clusters as well as dislocation loops of small radius [1]. However, the study of dot defects (vacancies, interstitial atoms, antistructural defects), which drastically affect optical and electrical properties, is of the greatest interest. Unfortunately, the presence of dot defects in a crystal lattice generally renders an insignificant effect on the character of X-ray scattering. The use of quasi-forbidden reflections in binary crystals essentially enhances the capabilities of the study of structure defects, caused by inhomogeneity of a chemical composition [2–4]. The aim of this paper is to review the results obtained recently in this field of research, also to analyse features of the X-ray diffraction for the

quasi-forbidden reflections and to develop further experimental procedures of the control of crystal nonstoichiometry.

2. LITERATURE REVIEW

Let us consider the basic diffraction effects, which arise in a distorted crystal medium. Dynamic and kinematic approaches in the analysis of the specified effects are distinguished in the theory of radiation scattering by crystals. In the first case, it is essential to take into consideration the interaction of incident and scattered waves, which take place in high perfect crystals. The kinematic approach is used in rather distorted mosaic crystals containing high dislocation density. Within the framework of the kinematic approach analysed in detail by Krivoglaz [5], the following basic diffraction effects in a distorted crystal lattice are considered. In comparison with a perfect crystal, the intensities of diffraction peaks I_R are attenuated proportionally to the static Debye–Waller factor $\exp(-L)$, their angular location is displaced due to formation of the crystal lattice, averaged by displacements, and a diffuse background arises. Its intensity I_D depends on a character of strain fields, type and concentration of defects. The separate analysis of evolution of the diffraction peaks and diffuse background at variation of the defect structure of the crystal allows us to determine the most important diffraction parameters, characteristics of fields of strain, type of defects (size, concentration). The total intensity $I_\Sigma^K = I_R + I_D$, scattered by a crystal, does not depend on the characteristics of the crystal.

Unlike the kinematic case, the total intensity in the case of the dynamic scattering by the perfect crystal I_Σ^R, which, according to Molodkin [6], also consists of Bragg and diffuse components and is a function of the structural perfection of the crystal. The intensity, scattered by the real crystal I_Σ^R, as a rule, is within a range between two discussed cases of ideal-mosaic crystal I_Σ^K and ideal crystal I_Σ^D ($I_\Sigma^K > I_\Sigma^R > I_\Sigma^D$). Analysing I_Σ^R, the basic characteristics of structural perfection ($\exp(-L)$ and the coefficient of energy loss due to diffuse scattering μ_{ds}) can be determined. In binary crystals I_Σ^R depends also on the characteristics of homogeneity of chemical composition (concentration and size of components precipitates, degree of deviation of a composition from the stoichiometric one, $(c_\alpha - c_\beta)/c_\alpha$, where c_i is an effective concentration of a component in the crystal). Thus, if it is necessary to determine structural perfection parameters in real crystals, it is more complicated, as all the defects set forth above render an effect on the intensity of diffracted X-rays.

A unique, but rather simple procedure of dot defects study (deviation from stoichiometry) in A_3B_5 crystals was described recently [2, 7]. Fujimoto [2] proposed to use measurement of the integral intensity of Bragg diffraction beam at quasi-forbidden reflection 200 in GaAs crys-

tals. The geometrical factor of this reflection can be expressed through concentrations of components in sublattices c_{Ga} and c_{As}:

$$F_{200} = 4[c_{Ga}(f+f'+if'')_{Ga}\exp(-M_{Ga}) - c_{As}(f+f'+if'')_{As}\exp(-M_{As})], \quad (1)$$

where fi, f_i', and f_i'' are atomic formfactors of the i-th component and their corrections for anomalous dispersion, and M_i is Debye–Waller temperature factor. As $f_{Ga} \approx f_{As}$, their difference is close to one and insignificant changes in concentrations $c_i(c_{Ga} - c_{As})/c_{As} = 2.5 \cdot 10^{-5}$ can cause significant variations of the intensity (0.1%) for various radiations.

Due to the fact that the geometrical factor F_{200} is small for a number of characteristic wavelengths (CuK_α, MoK_α, AgK_α), and also due to the influence of other diffraction parameters, the distinction between quantities of the integral intensities calculated in the approach of the scattering by the perfect and mosaic crystal is insignificant. The ratio of these quantities I_Σ^K/I_Σ^D for the specified wavelengths for quasi-forbidden reflex 200 is equal accordingly 1.10, 1.01, and 1.03. At the same time such ratios for reflex 400 (structural) are accordingly equal 7.0, 3.9, 5.5. It follows from this that the structure defects do not have a significant effect on the intensity of diffraction peak 200, that creates favourable conditions for the study of deviations from stoichiometry. Therefore, composition studies can be performed both in perfect and in real crystals, containing, for example, dislocations. In this connection it is interesting to note that in [3], as well as in [8], the correlation between the character of dislocation density distribution and quantity $c_{As} - c_{Ga}$ was observed (see Fig. 1). Similar profiles were observed by the authors for other physical properties (resistivity, mobility, photoluminescence). The indicated facts specify the connection of deviations from stoichiometry with the parameters mentioned above. However, correlation between the dislocation density and nonstoichiometry parameter can also be interpreted as an increase of the initial extinction in the crystal. The dependence of the integral intensity distribution of quasi-forbidden reflections on the dislocation density was investigated [9]. The dependence of the integral intensity distribution obtained in this work can be explained based on enrichments of the crystal lattice by an anionic component with the increase of the dislocation density, taking into account an opposite correlation of values of the scattering factors of A- and B-sublattices in GaAs and InAs. These results are the direct proof of the influence of the stoichiometry change on the intensity of quasi-forbidden reflections.

A criterion for transition from the dynamic to kinematic mode of X-ray scattering for quasi-forbidden reflections was established in [10]. It was shown therewith that at dislocation densities $\sim 10^3$ cm^{-2} in GaAs crystals the scattering is described by the kinematic theory. It has allowed us to use the formula of the kinematic theory of X-ray scattering in further calculations.

The authors of [11] attempted to study an effect of an elastic bending on the integral intensity of quasi-forbidden reflections. The basic result of the study is the taking into account the influence of dot defects distribution under the action of elastic strains fields on the integral intensity of quasi-forbidden reflections.

The analysis of these works has shown that despite the visual physical interpretation of obtained results, there are some difficulties in the case of the nonstoichiometry parameter determination without the taking into account the model of solid solution.

Theoretical dependences of the integral intensity of quasi-forbidden reflexes on stoichiometry deviations (type of dot defects, their concentration and localization in the lattice) and diffraction conditions were calculated based on conclusions of the kinematic theory of X-rays Bragg scattering [8]. It was shown that these dependences have linear character and essentially differ for Schottky and Frenkel defects. In the latter case the tangent of a slope angle of the straight line $I_{\Sigma}^{R} = f(c_{\alpha} - c_{\beta})$ depends on the location of interstitial atoms in non-equivalent pores of the sphalerite lattice.

It was noted by Fukumachi [12] for Bragg case and in [13] for Laue case that the sensitivity to minor deviations from the stoichiometric

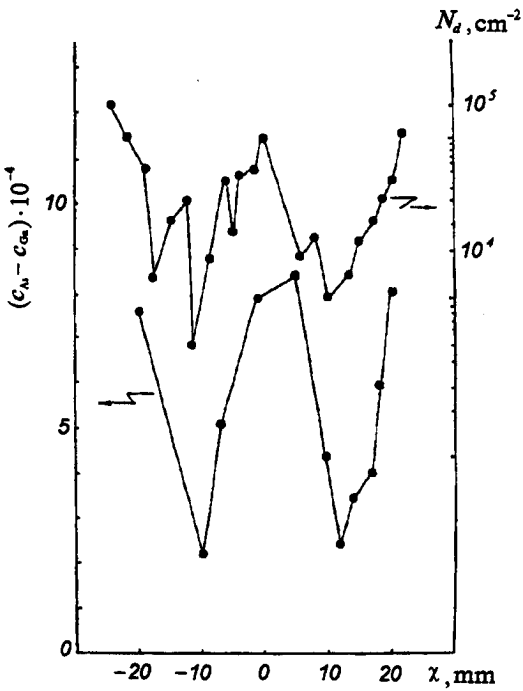

Figure 1. Correlation in the dislocation density N_d distribution and nonstoichiometry parameter along GaAs plate [2].

composition can be additionally increased using wavelengths where the effect of the anomalous dispersion is significant.

The following comments are necessary concerning features of the radiation scattering near *K*-edges of absorption in the case of Laue-diffraction described in [13]. Firstly, precise values of the dispersion corrections for functions of the atomic scattering f for various wavelengths are not available, that makes an estimation of the nonstoichiometry difficult. Secondly, as the corrections Δf near λ_k can reach big values, F_h for such wavelengths can sharply decrease, that will mean an increase of extinction length up to the size of a sample t_0. This means the transition of the scattering to the kinematic mode and, hence, losses of sensitivity to structural defects. This fact allows us to interpret precisely the results of the analysis of the nonstoichiometry of monocrystals. However, complications of the intensity measurement with the precision of ~ 0.01%, an influence of multiwave peaks and multiple harmonics make this method practically unsuitable for quantitative evaluation of the crystals nonstoichiometry. To control the nonstoichiometry, the geometry of reflection (Bragg case) is preferable due to a number of reasons. At first, the implementation of $\mu t < 1$ condition in Laue geometry is connected with substantial technical difficulties (production of thin $t_0 = 50$ μm, especially high absorption crystals). Secondly, the increase of crystals thickness results in the correlation $t/\Lambda >> 1$, where Λ is the extinction length, and the integral intensity will be a function of structural perfection of the crystal.

3. ADVANCED TECHNIQUE OF THE NONSTOICHIOMETRY CONTROL

In this study the procedure free from these disadvantages is proposed. For quasi-forbidden reflections of the type $h + k + l = 4n + 2$ ($n = 0, 1, 2...$; hkl are Miller indices) the expression for F_h in a stoichiometric binary crystal AB becomes

$$F_h = 4[(f_A - f_B + \Delta f_A' - \Delta f_B') + i(\Delta f_A'' - \Delta f_B'')]. \quad (2)$$

Using (1) and (2), the expression for the normalized integral intensity can be written for kinematic approach as

$$I = 16[(f_A - f_B + \Delta f_A' - \Delta f_B')^2 + (\Delta f_A'' - \Delta f_B'')]^2. \quad (3)$$

Let us consider now the expression for F_h and intensity for the case of crystals with Schottky defects at excess of A component ($AB_{1-x}[V_B]_x$) [8]:

$$F_h = 4[(f_A - (1 - x)f_B], \quad (4)$$

$$I = 16\{[f_A - f_B + \Delta f_A' - \Delta f_B' + x(f_B + \Delta f_B')]^2 + [\Delta f_A'' - \Delta f_B'' + x\Delta f_B'']^2\}, \quad (5)$$

where x is vacancy concentration of B component.

As the dispersion corrections are functions of X-ray wavelength, the integral intensity will be a function of the wavelength and concentration of defects. The calculation of dependence $I = f(\lambda, x)$ was performed within a wide range of wavelengths, including K-edges of absorption of GaAs crystals components. The values of atomic scattering functions from [14] were used in calculations, and the dispersion corrections were calculated by Khenl formula.

The dependence of the integral intensity as a function of the wavelength for different vacancy concentrations As in GaAs is presented in Fig. 2. The analysis of the dependences (see the inserts in Fig. 2) shows that the location of the intensity minimum in a short-wave range of K-edge of absorption is sensitive to the change of the crystal stoichiometry. The calculation shows that the change of the vacancy concentration of As by 1% results in the displacement of location of the intensity minimum near K-edge by 0.01Å. It also follows from Fig. 1 that the presence of vacancies in the crystal displaces minima of an intensity near K-edge of Ga and As in opposite directions in relation to the stoichiometric direction. Therefore, the sensitivity of the method is considerably increased at measurement of distance between intensity minima in short-wave ranges of K-edges of ab-

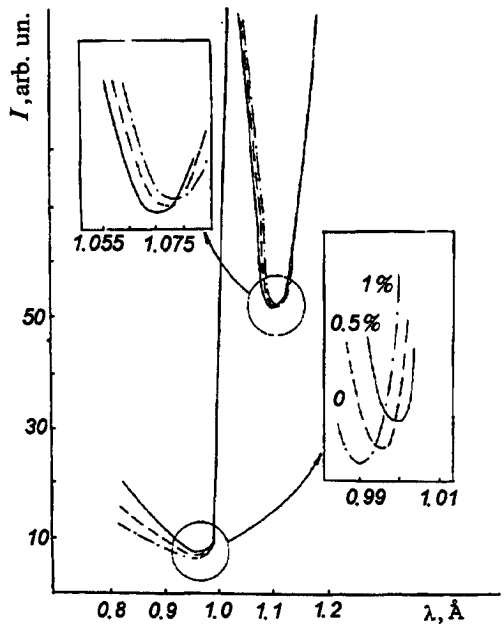

Figure 2. Dependence of the intensity on the wavelength and arsenic vacancy concentration near K-edges of absorption of GaAs.

sorption. The dependence of change of location of the intensity minimum near *K*-edge of absorption for As and changes of distance between minima on As-vacancy concentration in the crystal are presented in Fig. 3. The calculation shows that locations of intensity maximums in long-wave ranges of *K*-edges are low-sensitive to stoichiometry changes. This conclusion can be explained easily if one takes into account that the dispersion corrections in the short-wave range become commensurable with the atomic scattering functions, and in the long-wave range they decrease spasmodically.

Similar calculations were also carried out for other types of dot defects (interstitial atoms, antistructural defects and impurities).

Typical spectra of the intensity distribution near *K*-edges of absorption of GaAs atoms as functions of the wavelengths measured in various areas of the crystal are presented in Fig. 4.

The behaviour of dot defects in various binary compounds was investigated using the methods described above. In particular, the effect of the laser IR-irradiation on transformation in a system of dot defects in semiconductor crystals of GaAs and InAs was studied [15]. The influence of machining of monocrystals surface on dot defects distribution along the working area (effect of the long-range action) was studied [7].

4. CONCLUSIONS

Thus, the proposed procedure of the control of the monocrystals non-

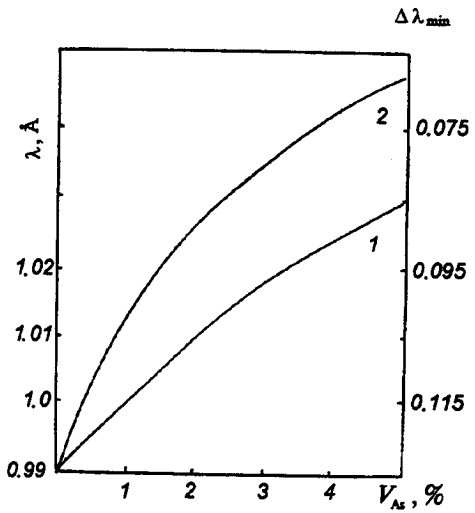

Figure 3. Dependence of change of the intensity minimum location near *K*-edges of absorption of As (*1*) and distance between minima (*2*) on As-vacancies concentration.

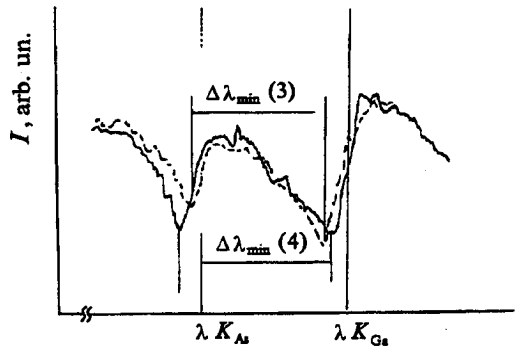

Figure 4. Experimental spectra of the intensity distribution near *K*-edges of absorption of GaAs, taken in different areas of the crystal.

stoichiometry has a lot of advantages: it excludes an operation of the integral intensity measurement with a precision of 0.01%, and it eliminates complexities connected with the influence of multiwave peaks and multiple harmonics on the intensity. The precision of nonstoichiometry parameter determination is not less than that for the previously known methods and is, in particular, for GaAs $(c_{As} - c_{Ga})/c_{As} = 1.3 \cdot 10^{-5}$. The Bragg variant of the procedure, as already noted, is preferable. At first, by the reasons which have been mentioned above. Secondly, in spite the fact that for some semiconductors the ratio $I_{\Sigma}^{K}/I_{\Sigma}^{D}$ (in particular for InP, GaP, and InAs) is much more than for GaAs, the parameter $t_{pen}/\Lambda < 1$ ($t_{pen} = 1/\mu$ is the depth of X-rays penetration into the crystal) due to the greater value of the normal photoelectric absorption coefficient μ. Hence, X-ray scattering is described by the kinematic approach. It considerably expands the circle of materials under investigation.

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