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Effect of Structure Perfection of Polar Crystals on Friedel Intensity Ratio for X-Ray Reflections in the Region of Resonant Frequencies

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An effect of the structure defects in GaAs and GaP crystals on the Friedel pairs' intensity ratio, $r = R_{333}/R_{\bar{3}\bar{3}\bar{3}}$, for the polar sensitive reflections is shown theoretically and experimentally by using energy-dispersive diffractometry. It is explained by the diffuse scattering of X-rays from regions distorted by defects in crystal. Dependence of the r value for the nonpolar quasi-forbidden 222 reflection is revealed and supposed to be connected with a diffuse-scattering component of reflectivities from centrosymmetrical reflections.

Експериментально з допомогою енергодисперсивної дифрактометрії та розрахунковим шляхом показано вплив структурних дефектів на величину фриделівського відношення інтенсивностей полярночутливих 333 рефлексів $r = R_{333}/R_{\bar{3}\bar{3}\bar{3}}$, пов'язаних з дифузним розсіянням у спотворених областях в кристалах GaAs і GaP. Знайдено структурну та полярночутливу залежність величини r для неполярного квазізабороненого 222 відбиття, яке, ймовірно, пояснюється вкладом дифузного розсіяння від нецентросиметричних рефлексів.

Экспериментально с помощью энергодисперсивной дифрактометрии и расчетным путем показано влияние структурных дефектов на величину фриделевского отношения интенсивностей полярночувствительных 333 рефлексов $r = R_{333}/R_{\bar{3}\bar{3}\bar{3}}$, связанное с диффузным рассеянием на искаженных областях в кристаллах GaAs и GaP. Обнаружена структурная и полярночувствительная зависимость величины r для неполярного квазизапрещенного 222 отражения, которая предположительно объясняется вкладом диффузного рассеяния от нецентросимметричных рефлексов.

Key words: quasi-forbidden reflection, Friedel intensity ratio, resonant frequencies, reflectivity.

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1. INTRODUCTION

The dynamical Bragg diffraction peculiarities were studied for centrosymmetrical [1—3] as well for the polar A^3B^5 perfect crystals [4—7]. It was done due to the fundamental point of view and also in particular for the need of solid state electronics in the polar A and B surface identification. The intensity ratio of Friedel pair intensities in conditions of the Bragg diffraction was shown [7] as follows:

$$r_h = \frac{R_{ih}}{R_{i\bar{h}}} = \frac{|F_h|^2}{|F_{i\bar{h}}|^2}, \tag{1}$$

taking into account the anomalous dispersion phenomena. It was assumed that this ratio is independent of structure state of the crystal media (a perfect or ideal-mosaic crystal). The effect of crystal polarity is especially essential in the wave region of X-rays close to the absorption K-edges of the components. The ratio (1) was experimentally investigated for near perfect GaSb and InAs crystals [7] and it found to be violated due to a secondary extinction. The attempts in the papers [4, 5] were made for determination of the absolute crystallographic polarity by measuring of the intensity jumps close to the absorption K-edges in binary crystals. The influence of the thermal lattice vibrations on the relation (1) was investigated in [8]. It can be characterised by the dynamical Debye—Waller factor M, which turned out to give important contribution to the ratio (1). This fact leads to the conception that the static Debye—Waller factor L describing the effect of structure distortions should be taken into account by consideration of the Friedel intensity ratio (1) in actual crystal. One should also note the importance of the parameter L influence on a susceptibility of material [9, 10].

Investigation of the behaviour of the integral reflectivity (IR) under the resonant condition of fluorescent radiation, especially for polar reflections, as well as mechanism of its effect to the diffraction of X-rays seems to be important. It is known that the IR of so called quasi-forbidden reflections (QFR) is not sensitive to crystal polarity.

The aim of this paper is to study the Bragg diffracted beam behaviour of intensities in the region of resonant frequencies ω for noncentrosymmetric (polar) and weak, QFR, reflections in A^3B^5 binary actual crystals (GaAs, GaP) as well as study the influence of structure imperfection on the Friedel ratio near the absorption *K*-edges.

2. THEORETICAL BASIS

The IR for the Bragg case of diffraction in an actual crystal may be represented as a sum of coherent (R_{iB}) and diffuse (R_{iD}) components [10]:

$$R_i = R_{iB} + R_{iD}. \tag{2}$$

Following [11, 12], let us consider the main results of the scattering theory for the arbitrary relation between the real and imaginary parts of a structure factor including the case when the real part of a susceptibility is equal to zero, $\chi_{rh} = 0$. The corresponding parts of χ, *i.e.* χ_{rh} and χ_{ih} determining the (R_{iB}) and (R_{iD}) in (2) are known to be described by the following expressions:

$$\chi_{rh} = -(4\pi/V\cdot\omega^2)\sum_j (f_j^0 + f_j')\exp(i2\pi\bar{h}\cdot\bar{r}_j)M_j, \tag{3}$$

$$\chi_{ih} = -(4\pi/V\cdot\omega^2)\sum_j (f_j')\exp(i2\pi\bar{h}\cdot\bar{r}_j)M_j, \tag{4}$$

where M_j, $\bar{h}$, $\bar{r}_j$, V, f stand for dynamical Debye–Waller factor, diffraction vector, radius-vector, volume of elementary cell, and atomic form-factor respectively. The phase difference δ between these components of χ_h is written as

$$\delta = \alpha_{ih} - \alpha_{rh}. \tag{5}$$

Then the important in the analysis product of χ_h and $\chi_{\bar{h}}$ values in a noncentrosymmetrical crystal using in a dynamical theory [1, 9] may be written as:

$$\chi_h\chi_{\bar{h}} = |\chi_h|^2(1 - b^2 + i2p\cos\delta). \tag{6}$$

Here

$$|\chi_h|^2 = |\chi_{rh}|^2 + |\chi_{ih}|^2, \quad b = \sqrt{2}\,|\chi_{ih}|/|\chi_h|, \quad p = |\chi_{rh}||\chi_{ih}|/|\chi_h|^2. \tag{7}$$

One can see from these expressions, the parameter b is equal to zero when $\chi_{ih} = 0$ and its maximum value $b = \sqrt{2}$ in the case of $\chi_{rh} = 0$. The resonant factor W characterising the deviation of diffraction conditions from the exact Bragg position of a sample depends on some geometrical factors (see the Fig. 1):

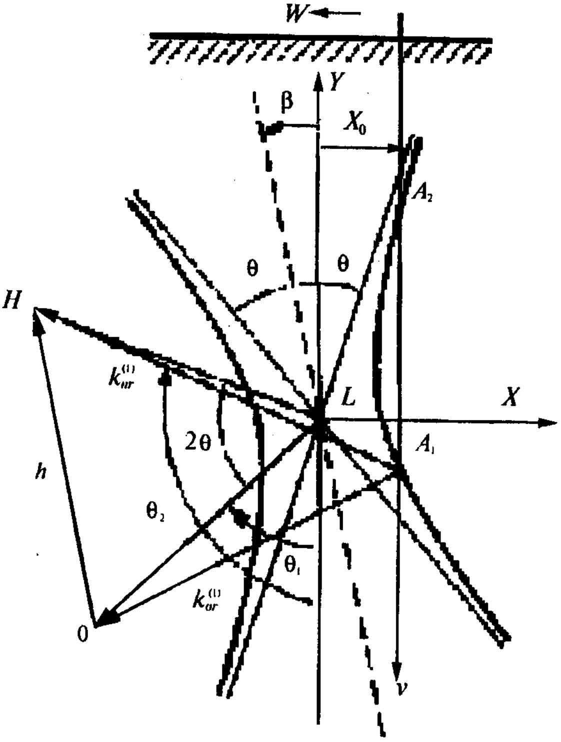

Fig. 1. Dispersion surface in reciprocal space for the Bragg case of diffraction. The dotted line passing the Laue point L denotes the diffraction plane trace; ν is a normal to a surface intersecting the right branch in two tie points, A_1 and A_2. The angle β depicts deviation of the diffraction scheme from symmetrical case.

$$W = -X_0(\sin 2\vartheta)/[|(\cos\vartheta_1)(\cos\vartheta_2)|^{1/2} k_{or}|\chi_h|]. \tag{8}$$

For simplification of this expression let us introduce the following notations:

$$g = \chi_{i0}/|\chi_h|, \tag{9}$$

$$g' = g(\sin\vartheta)(\cos\beta)/|(\cos\vartheta_1)(\cos\vartheta_2)|^{1/2}. \tag{10}$$

Following the notations used in [11] we will write the expression for the differential coefficient of reflection, *i.e.* the ratio P_h/P_0 of intensities for the incident and diffracted beams in the Bragg case of diffraction:

$$P_h/P_0 = k[\Pi - (\Pi^2 - 1)^{1/2}], \tag{11}$$

where

$$k = (1 - 2p\sin\delta)/[(1 - b^2)^2 + 4p^2\cos^2\delta]^{1/2},$$

and

$$\Pi = \frac{[(A^2 + B^2)^{1/2} + W^2 + g'^2]}{(1 - b^2)^2 + 4p^2\cos^2\delta]^{1/2}}. \tag{12}$$

The values A and B in (12) are equal respectively:

$$A = W^2 - 1 - g'^2 + b^2, \tag{13}$$

$$B = 2(g'W - p\cos\delta). \tag{14}$$

The intensities of diffracted beams from the opposite sides of a polar crystal will differ due to phase factor $2p\sin\delta$. So, when $\chi_{rh} = 0$, P_h/P_0 is written as follows:

$$P_h/P_0 = l - (l^2 - 1)^{1/2}, \tag{15}$$

where

$$l = [(W^2 - 1 - g'^2)^2 + 4g'^2W^2]^{1/2} + W^2 + g'^2. \tag{16}$$

When $\chi_{rh} = 0$ the ratio (15) does not depend on polarity. The reflection curve for symmetrical case of diffraction ($\beta = 0$) has the maximum equal to unity at the exact Bragg position ($W = 0$). The intensity of polar reflection is determined considerably by phase factor. The corresponding phase factors for polar and nonpolar reflections in binary crystals have the following forms respectively:

$$\delta_{\pm(111)} = \pm\mathrm{tg}^{-1}\frac{(f^0_{\mathrm{As}} + f'_{\mathrm{As}} \pm f''_{\mathrm{Ga}})}{(f^0_{\mathrm{Ga}} + f'_{\mathrm{Ga}} \pm f''_{\mathrm{As}})},$$
$$\delta_{\pm(200)} = \mathrm{tg}^{-1}\frac{(f''_{\mathrm{Ga}} - f''_{\mathrm{As}})}{(f^0_{\mathrm{Ga}} + f'_{\mathrm{Ga}} - f^0_{\mathrm{As}} - f'_{\mathrm{As}})}. \tag{17}$$

The dependences of the phase δ as a function of the wave length near the Ga and As absorption K-edges are shown for a GaAs crystal in Fig. 2. One can see the most considerable phase variations happen just near the λ_{As} and λ_{Ga}. For the 111 and $\bar{1}\bar{1}\bar{1}$ reflections, these variations occur in the opposite directions and the intervals of their changes are different.

Formulas (2)–(15) for a perfect crystal may be generalized for the case of imperfect crystal with homogeneously distributed defects. According to results of the dynamical theory [1, 2] the Fourier compo-

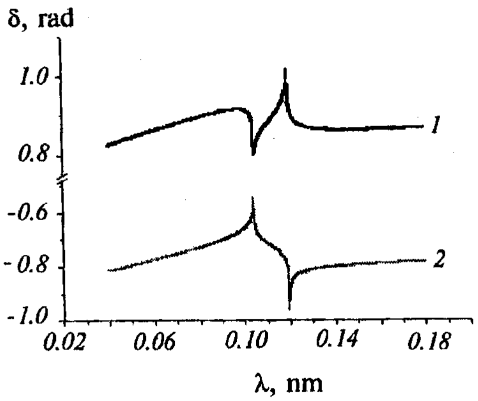

Fig. 2. Energy dependences of the structural-factor phase, δ, between two absorption *K*-edges, *i.e.* As (λ_{As} = 1.045 Å) and Ga (λ_{Ga} = 1.1957 Å), for 111 (*1*), $\bar{1}\bar{1}\bar{1}$ (*2*) reflections.

nents of susceptibility for a perfect crystal should be replaced in a real crystal by the renormalized values which may be represented as:

$$\tilde{\chi}_h = \chi_h E, \quad |\tilde{\chi}_{i0}| = |\chi_{i0}| + \overset{0}{\mu}_{DS}/K. \tag{18}$$

Here, $K = 2\pi/\lambda$, $E = \exp(-L_h)$, $\overset{0}{\mu}_{DS}$ stand respectively for the wave vector, Debye–Waller static factor and a coefficient of the IR coherent component weakening due to transition of part of strong wave intensity in a background. The second term in (18) characterizes the sensitivity of the absorption parameter g (9) to structure defects via the structure sensitive characteristics E and $\overset{0}{\mu}_{DS}$.

The expression for the IR diffuse component according to [3] has the following form:

$$R_{iD} = R_{iK}\Pi(t)(1 - E^2), \tag{19}$$

where $R_{iK} = C^2 Qt/\gamma_0$ characterises the reflectivity of an ideal-mosaic crystal with thickness t and ϑ is this value related to unit length. Here C, ϑ, γ_0 and γ_h stand for a polarisation factor, Bragg angle and cosines of it for an incident and reflected beam respectively, $\mu_0 = 2\pi|\chi_{i0}|/\lambda$ is a linear coefficient of photoelectric absorption. The factor $\Pi(t)$ is also a function of the characteristic $\overset{0}{\mu}_{DS}$ being similar to the parameter of secondary extinction [2, 3, 5].

The expression for polarity expression, r_h (1) may be written in the case of a real crystal as follows:

$$\tilde{r}_h = R_{iH}/R_{i\bar{H}} = [R_{iP}P(t,g,\kappa)E + R_{iK}\Pi(t)(1-E^2)]/[\bar{R}_{iP}P(t,g,\kappa)E + \bar{R}_{iK}\Pi(t)(1-E^2)], \tag{20}$$

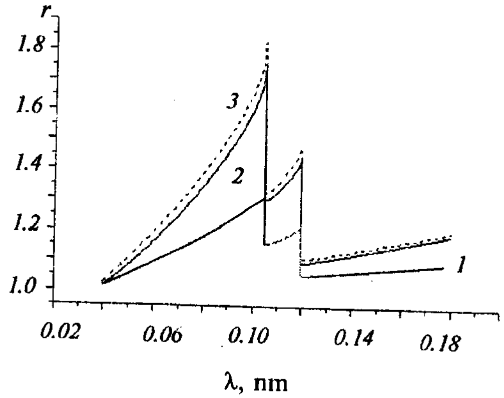

Fig. 3. Friedel intensity ratios r for h- and $\bar{h}$-reflections in the region of the absorption K-edges in GaAs. 111 reflection for ideal (*1*), real (*2*), and ideal-mosaic crystals (*3*).

where $R_{iP}=16(3\pi)^{-1}Q\Lambda/\gamma_0$ and $\Lambda=\lambda(\gamma_0|\gamma_h|)^{1/2}(C|\chi_{rh}|)^{-1}$ is an extinction length. The parameters relating for a perfect and ideal mosaic (kinematical) crystals are designated by the P and K indexes respectively. The Friedel ratio for an actual crystal is more complicated as comparing with the cases of a perfect or ideal-mosaic crystals. It follows directly from the formula (20). Scattering by an actual crystal can be carried out by introduction of the parameters E and μ_{ds} without any restriction of their values. This leads to the result shown in Fig. 3, which shows the sensitivity of the polarity characteristic r to structure perfection of a crystal.

3. EXPERIMENTAL

The actual crystals of the A^3B^5 compounds, *i.e.* GaAs and GaP with 111 orientation of a surface were chosen for investigations. They had $2{\cdot}10^4\,\text{cm}^{-2}$ dislocation density according to the etch pits account method. All of the measurements in this paper were carried out by means of a single-crystal spectrometer (SCS) using the energy-dispersive method of intensity registration. The divergence of diffracted beams as determined by the method [13] was not higher than $\Delta\lambda=0.0003$ Å. The spectral dependence of the intensity in the Bragg case of diffraction were measured by the known method of $\theta-2\theta$ scanning. The Si(Li) solid detector with energy resolution ~100 eV was used for registration of an intensity.

Characteristic distribution of the X-ray diffracted beams on energies for the acting 111 reflection in a GaAs crystal is shown in the Fig. 4. One can see the peak for 111 acting reflection for a fixed value of the

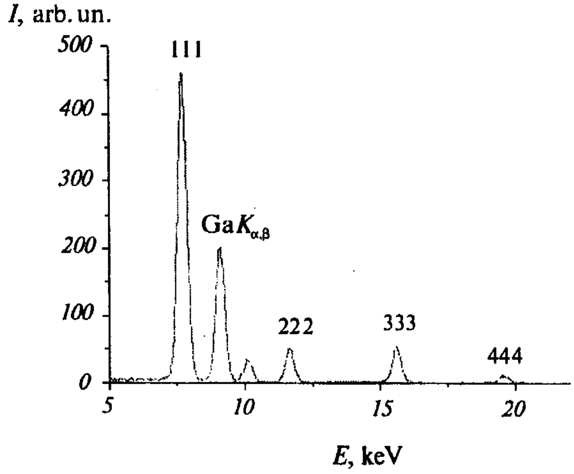

Fig. 4. Energy spectrum of the diffraction reflection 111 in GaP. Ga$K_{\alpha,\beta}$ are the gallium fluorescent peaks.

Bragg angle as well as fluorescent peaks from the atoms of both sublattices (the PK-fluoresce lines are outside the energy scale of the figure). The working regime of X-ray tube (U = 50 keV, I = 35 mA) permitted the presence of high-energy λ/n harmonics for higher orders of reflection. So the several peaks (111, 222, 333) were observed by continuous scanning of a crystal in a wide angle interval. The measurements were carried in a wide angle interval including the regions near the absorption K-edges both for the positive and negative Miller indexes. For every reflection at last 300 experimental values of an intensity were registered. The counting time in every point was chosen to reach the statistical accuracy not worse than 1% for every reflection. Calculation of reflectivities was carried out according to [14].

4. RESULTS AND THEIR DISCUSSION

The experimental energy distributions of r_h are shown in the Figs. 5, 6 for the noncentrosymmetric 333 and for nonpolar quasi-forbidden 222 reflections of GaP crystal with dislocations. The common feature of these reflections is different character of an intensity behaviour for the hkl and $\bar{h}\bar{k}\bar{l}$ Friedel pair reflections. As a result of this, the r value for both of the reflection is distinct from unity. This circumstance for the polar sensitive 333 reflection, as it well known, is connected with violation of the Friedel law [9]. The calculated values of this parameter obtained for the cases of an ideal-mosaic and perfect crystal (the curves *1* and *2*) are in qualitative agreement with experimental data. Sensitivity of the parameter r to defects, which in a crystal can be set by the

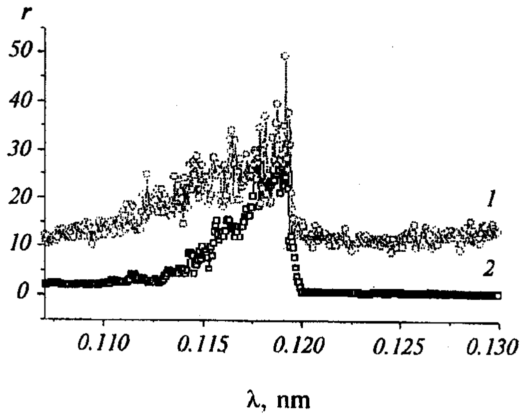

Fig. 5. Experimental intensity ratios for Friedel pairs of the 333 reflection near Ga absorption *K*-edge; ideal-mosaic (*1*), perfect (*2*) GaP crystals.

Debye–Waller factor L in (18), was discovered not only for the wavelength region situated between the absorption *K*-edges but in the distant parts of continuous spectrum. This fact is in contradiction with early [5] and more late results about non-sensitivity of the Friedel ratio to defect structure.

Deviation of the r parameter from unity for centrosymmetrical quasi-forbidden 222 reflection (Fig. 6) can not be explained however by existing ideas [7, 9, 14]. Really as it follows from (20), the $R_{ih}/R_{i\bar{h}}$ ratio should not deviate from unity even in an actual crystal where the diffuse component of reflectivity exists. But one can see a considerable deviation of the polarity parameter from the unity in the Fig. 6 where the experimental energy dependence of r_{222} in an actual GaP crystal is shown. This deviation is noticeable especially near the gallium absorption *K*-edge (effect of anomalous sensitivity of diffraction of quasi-forbidden reflection to polarity).

Let us discuss now the possible mechanism of discovered anomalous sensitivity of centrosymmetrical 222 reflection to polarity of 111 planes in GaP crystal. PK_α as well as GaK_α fluorescent radiation can not affect on this phenomena because the energy dispersive system of intensity registration allows to get rid of detrimental components of continuous spectrum. So one should suppose that some contribution of diffuse scattering of the same wavelength from distorted regions near defects (dislocation) from 111 plans can take place by registration of the 222 reflectivity at the corresponding channel of the analyser. That is why the diffuse components of scattering on the mentioned wavelength from polarsensitive planes (111, 333, *etc.*) can entrance the detector slit.

Relativity low values of r, which is characteristic for a crystal with a distorted surface due to lapping, as compared with that one chemically

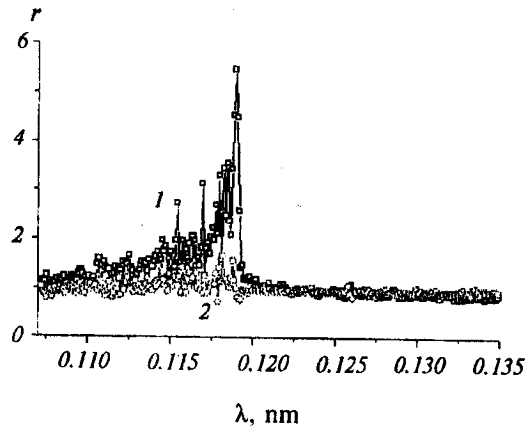

Fig. 6. Experimental dependences of intensity ratios for the 222 reflection in GaP near the Ga absorption *K*-edge. The specimen with perfect structure (*1*), ideal-mosaic (lapped) crystal (*2*).

polished sample (an observation made early also by the other mentioned authors), are connected perhaps with very wide rocking curve for mosaic crystal. This can not be measured by a detector with narrow slit.

5. CONCLUSIONS

1. The sensitivity of the intensity ratio of a Friedel pair of reflections near the absorption edge to structure defects in GaAs and GaP binary crystals due to diffuse scattering of X-rays was shown experimentally and by calculation.
2. Anomalous sensitivity of intensity ratio to structure imperfections was discovered for the centrosymmetrical quasi-forbidden 222 reflection in GaP crystal connected supposedly with polar reflection contribution of diffuse scattering on distorted regions near defects.

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