Photoeffect Under the Conditions of Dynamical X-ray Diffraction*

By M. V. Koval'chuk and I. A. Vartanyantz

Institute of Crystallography of the Academy of Sciences of the USSR, Leninsky prospect 59, Moscow 117333, USSR

and V. G. Kohn

I. V. Kurchatov Institute of Atomic Energy, Kurchatov Square 46, Moscow 123182, USSR

Abstract

The applications of the external photoeffect excited by an X-ray standing wave to structure studies of crystal subsurface layers are discussed. In experiments conducted with an epitaxial Si film doped with B and Ge, with Ge concentrations ranging from $3 \cdot 7 \times 10^{19}$ to $1 \cdot 5 \times 10^{20}$ atoms cm^{-3}, a change of phase of the scattering amplitude on the photoemission curve is found. This change is caused by the total surface displacement due to a change in the interplanar spacing in the disturbed layer. The experimental results are compared with accurate theoretical calculations in a bicrystal model. Values for the phase $\varphi(0)$ and degree of amorphization $\exp[W(0)]$ on the surface are obtained by least-squares fitting. Universal analytical formulae for the computation of functions describing electron transport and the escape depth of electrons in a crystal are suggested. The potentialities of the depth-selective analysis of X-ray standing waves are analysed. The theoretical foundations of the secondary-radiation yield under the conditions of multiple diffraction are developed. A direct observation of an enhanced Borrmann effect in Laue multi-wave diffraction is predicted.

1. Introduction

One of P. P. Ewald's main contributions to the development of crystal physics was the formulation of the dynamical theory of X-ray diffraction, which predicted the formation of standing X-ray waves in a perfect crystal. For almost 50 years this wave existed only as a hypothesis. Batterman (1962) was the first to attempt to see the standing wave and its behaviour by observing the fluorescence radiation emitted by crystal atoms. Although the attempt was unsuccessful it stimulated the development of a new field in dynamical diffraction studies, dealing with the investigation and practical application of standing X-ray waves.

The first measurements were made in the Bragg diffraction scheme, which is best suited for crystal surface-layer studies. In the angular region of total diffraction reflection (TDR) of X-rays the incident wave is reflected by the surface layer with a thickness of the order of the extinction length L_{ex}. The L_{ex} values range from fractions of a micrometre to dozens of micrometres. The diffracted wave, interfering with the incident one, produces a peculiar radiation field structure with nodes and antinodes. The nodes and antinodes periodically repeat themselves in space. They form a standing wave with a period which is either exactly equal to the distance between the reflecting planes of the crystal or is less than this distance by a factor of an integer.

It is known that the photoelectron emission yield (the secondary radiation) is proportional to the intensity of X-rays at the atoms. Naturally, the secondary-radiation yield will depend on the mutual arrangement of atomic planes and standing-wave nodes. It is also known, from changing the incidence angle of an X-ray beam in the TDR region, that the positions of the standing-wave nodes continuously change. For instance, in silicon crystals the field nodes related to the smaller-angle side of the TDR are between the atoms, whereas for the greater-angle side they coincide with the atoms. The standing-wave motion leads to an anomalous angular dependence of the secondary-radiation yield with a minimum and a maximum on the borders of the TDR region.

It was just this dependence that Batterman expected to observe. However, the Ge $K\alpha$ fluorescence radiation yield curve turned out to be proportional to $(1 - P_R)$, where P_R is the X-ray reflection coefficient, and the standing-wave structure was hardly evident on the borders of the TDR region. This was because the depth of yield (L_y) of the fluorescence radiation exceeded by far the penetration depth of X-rays in the crystal. As a result, all the radiation absorbed in the crystal, the amount of which, following the law of conservation of energy,

is equal to $(1 - P_R)$, gives rise to a fluorescence signal. The secondary radiation yield is proportional to the wave-field intensity at the atoms only if the condition $L_y \ll L_{ex}$ is fulfilled. It was this condition that was not fulfilled in the experiment of Batterman.

The above-mentioned problem does not exist in measurements of the photoelectron emission since the electrons escape from a thin subsurface layer with a thickness of fractions of a micrometre. Already in the first works on the measurement of the photoelectron emission, carried out in the USSR in the early 70's (Shchemelev, Kruglov & Pronin, 1970; Shchemelev & Kruglov, 1972; Schemelev, Efimov & Kruglov, 1974), the anomalous angular dependence corresponding to the behaviour of an X-ray standing wave was observed. Later this field of research was developing intensively in the USSR, and at present dozens of papers on this subject have been published [for details see, for instance, a review by Koval'chuk & Kohn (1986)].

This paper considers new potentialities for using the photoelectron emission induced by an X-ray standing wave in structure studies of subsurface crystal layers. The results pertaining to the photoelectron emission are presented in § 2. § 3 deals with determining the probability function of photoelectron yield. The potentialities of depth-selective X-ray standing-wave analysis are considered in § 4. The formulation of the general theory of secondary-radiation yield under multiple diffraction conditions is presented in § 5.

2. Photoelectron emission in crystals with a disturbed surface layer

The general theory of the angular dependence of the secondary-radiation yield in a crystal with a disturbed surface layer was developed in a paper by Afanas'ev & Kohn (1978). If an X-ray plane wave in polarization state s ($s = \pi, \sigma$) falls on a crystal at an angle differing from the Bragg angle θ_B by a value $\Delta\theta$, then the photoelectron yield from the ν-atom shell is determined by the formula

$$N_\nu^{(s)}(\Delta\theta) = \int_0^t dz P_\nu(z) \frac{dN_\nu^{(s)}(z, \Delta\theta)}{dz}, \quad (1)$$

where t is the crystal thickness, $P_\nu(z)$ is the function describing the electron transport (the probability of the electron penetrating from depth z to the crystal surface for electrons of the νth group), and the function

$$\frac{dN_\nu^{(s)}(z, \Delta\theta)}{dz} = \frac{c}{8\pi} \frac{\mu_{0\nu}}{\hbar\omega} (|E_{0s}|^2 + |E_{hs}|^2$$

$$+ 2 \operatorname{Re} \{E_{0s}^* E_{hs}[\chi_{ih}^{(s)}(\nu)/\chi_{i0}(\nu)]$$

$$\times \exp[i\varphi(z)]\} \exp[-W(z)]) \quad (2)$$

determines the number of X-ray quanta absorbed with consequent generation of electrons of the νth group at depth z in the crystal. In formula (2) $\mu_{0\nu} c/\omega = \chi_{i0}(\nu)$, $\chi_{i0}(\nu)$ and $\chi_{ih}^{(s)}(\nu)$ are the contributions of these processes to the Fourier transforms of the imaginary part of the crystal polarizability (together with the polarization factor), $\varphi(z) = \mathbf{hu}(z)$, $\mathbf{h}$ is the reciprocal-lattice vector, $\mathbf{u}(z)$ is the displacement of the atomic layer at depth z from its position in a non-disturbed crystal, and $\exp[-W(z)]$ is the static Debye–Waller factor which takes into account the random displacements of the atoms from a mean position at depth z.

The amplitudes of the incident E_{0s} and diffracted E_{hs} waves depend both on the angular deviation $\Delta\theta$ and on the coordinate z. In the general case these dependences are described by the Takagi–Taupin set of equations [Afanas'ev & Kohn (1978); see also formula (11)] or by a non-linear equation for the ratio of amplitudes E_{hs}/E_{0s} (Burgeat & Taupin, 1968; Kohn & Koval'chuk, 1981), if the plane spacing in the disturbed surface layer differs from that in the substrate by a value $\Delta d(z)$. In the substrate, where $\Delta d = 0$, the dependence of the amplitudes on z is exponential, $\exp[-\mu(\Delta\theta)z]$, where $\mu(\Delta\theta)$ is the effective absorption coefficient. Its maximum value is $\mu_{max} = 2/L_{ex}$.

The most interesting physical situation takes place if the condition $L_y \ll L \ll L_{ex}$ is fulfilled, where L is the thickness of the disturbed layer. In this case the z dependence of field amplitudes can be neglected. In the symmetrical Bragg geometry of diffraction the normalized photoelectron yield is described by the formula (for simplicity s and ν indices are omitted)

$$\kappa(\Delta\theta) = 1 + \frac{|E_h|^2}{|E_0|^2} + 2\frac{|E_h|}{|E_0|} f_c \cos[\alpha(\Delta\theta) + \phi_c], \quad (3)$$

where

$$f_c = \frac{|\chi_{ih}^{(s)}(\nu)|}{\chi_{i0}(\nu)} \exp(-W_A), \qquad \phi_c = \beta + \varphi_A, \quad (4)$$

$$\exp(i\varphi_A - W_A) = \frac{\int_0^t dz P(z) \exp[i\varphi(z) - W(z)]}{\int_0^t dz P(z)}. \quad (5)$$

In (3) and (4) $\alpha(\Delta\theta)$ and β are the phases of complex relations E_h/E_0 and $|\chi_{ih}|/\chi_{i0}$ (in a centrosymmetrical crystal $\beta = 0$).

According to (3), from the shape of the photoemission angular dependence curve in the TDR region one can readily determine two parameters characterizing different aspects of structure perfection of a subsurface layer with a thickness L_y. These are the so-called coherent position $\phi_c = \beta + \mathbf{hu}_A$, characterizing an average displacement of the atoms due to crystal lattice relaxation in the disturbed layer, and the coherent fraction f_c, which determines, in

particular, the number of atoms retaining regular positions in the diffracting plane.

Such a possibility was clearly demonstrated in the studies of germanium and gallium arsenide autoepitaxial films (Sozontov, Kruglov & Zakharov, 1979, 1981). However, analogous results for Si crystals have not been obtained so far. The reason is the small thickness of such films in Si and their small deformation. According to (5), to strengthen the influence of the film deformation on the curve shape, *i.e.* to make the standing-wave analysis more sensitive, higher reflection orders should be used. In such a case, on the one hand the phase φ_A becomes greater; on the other hand, the value L_{ex} increases, which is required for the condition $L \ll L_{ex}$ to be fulfilled.

In our experiments we used Si single crystals, doped with Sb up to a concentration of $3 \cdot 7 \times 10^{19}$ atoms cm^{-3}, covered with a grown autoepitaxial Si film doped with B up to a concentration of 10^{16} atoms cm^{-3} and with Ge. The concentration of Ge varies from sample to sample from $3 \cdot 7 \times 10^{19}$ to $1 \cdot 5 \times 10^{20}$ atoms cm^{-3}. The doping process was carried out so that the concentration of impurities was independent of z. The doping with Ge was made during the growth process by Ge reduction from germanium tetrachloride GeCl$_4$. The film thickness $L = 1 \cdot 5$ μm. Cu $K\alpha$ radiation ($\lambda = 0 \cdot 154$ nm) and a (444) nondispersional double-crystal diffraction arrangement with an asymmetric reflection in the monochromator (the angle between the incidence beam and the surface is 1°) were used. In this case $L_y = 0 \cdot 45$, $L_{ex} = 10 \cdot 5$ μm. Consequently, the condition $L_y \ll L \ll L_{ex}$ is fulfilled.
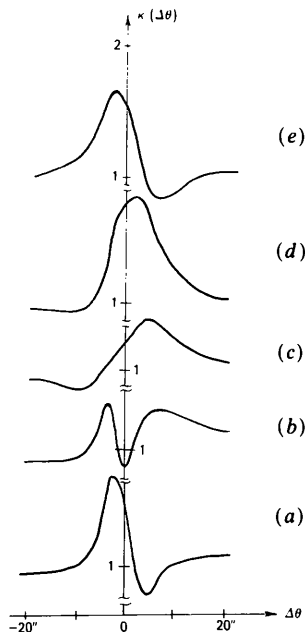

Fig. 1. Photoemission angular dependence for Si single crystals with autoepitaxial Si film, doped with B and Ge with Ge concentrations: (a) 0, (b) $3 \cdot 7 \times 10^{19}$, (c) 7×10^{19}, (d) 10^{20}, (e) $1 \cdot 5 \times 10^{20}$ atoms cm^{-3}.

Table 1. *Values of $\varphi(0)$ and $W(0)$ and the relative change of reflection-plane distance in a film $(\Delta d / d)$ for the experimental curves shown in Fig. 1*

The values of $\Delta d / d$ are obtained from the bicrystal model, $\Delta d / d = \varphi(0) d / 2 \pi L$.

Concentration of Ge (10^{19} atoms cm^{-3})	$W(0)$	$\varphi(0)/\pi$	$(\Delta d / d) \times 10^5$
0	0·51 (20)	−0·84 (20)	−2·2 (5)
3·7	0·25 (20)	−0·55 (20)	−1·4 (5)
7	0·8 (2)	−0·09 (20)	−0·2 (5)
10	0·8 (2)	0·37 (20)	0·9 (5)
15	0·79 (20)	1·36 (20)	3·6 (5)

The experimental results are presented in Fig. 1. The doping with Ge changes the plane spacing uniformly in the disturbed layer, which leads to a change of the surface displacement. Hence, the value of the phase φ_A, which in this case almost coincides with its value on the surface $\varphi(0)$, also changes. This factor, along with the change of parameter $W(0)$, is responsible for the variation of the shape of the curve. Table 1 presents the values of $\varphi(0)$ and $W(0)$ obtained by least-squares fitting of the experimental curves to the theoretical ones computed by using (3).

In conclusion, it should be noted that quite often the values of Δd in epitaxial films are independent of z throughout the entire film thickness. In this case the samples may be described theoretically as bicrystals. An analytical solution of the Tagaki–Taupin equations and an analytical expression for integral (1) with the exponential function $P(z)$ for the case of a bicrystal was obtained in Koval'chuk, Kohn & Lobanovich (1985). This solution allows one to compute the experimental results even in the case where the condition $L_y \ll L \ll L_{ex}$ is not fulfilled.

3. Electron transport

It follows from (1) that the quantitative analysis of photoelectrons emitted from the crystal does not only require a knowledge of the number of generated electrons excited by an X-ray standing wave at a crystal depth z. The function $P(z)$ describing the probability of experimental detection of these electrons should also be known. This function can be found provided the electron transport mechanism in a crystal with initial electron kinetic energy of several keV is known.

The problem of finding $P(z)$ is rather complicated owing to the statistical character of changes in the direction of electron motion and energy losses as a result of elastic and inelastic collisions. Until now, a linear approximation $P(z) = 0 \cdot 5(1 - z / L_y)$ was used for finding the function $P(z)$ in integral photoemission measurements (*i.e.* where all the electrons escaping from the crystal are detected regardless of their energies). Here the maximum escape depth of the electrons was determined from experiments on

the penetration of electrons with certain energies through thin films (Shchemelev & Kruglov, 1975). Apparently this approximation is rather rough, and the value of L_y is found from an experiment which is inadequate for the case considered.

In recent years a similar problem of the transport of electrons with energies of the order of several keV has been intensively developed in conversion electron Mössbauer spectroscopy (CEMS) [see Liljequist (1979) and references therein]. To determine the function $P(z)$ a Monte Carlo simulation method (MCSM) of elastic and inelastic collisions of electrons in a crystal was developed with an account of all the processes contributing to the result. This method was used for the computation of $P(z)$ in Fe, Al and Fe_2O_3 crystals.

In the same paper Liljequist (1979) also suggested a simple universal formula, approximating the computation results, which can be written as:

$$P(z) = 0.74[1 - 2.01(z/L_y) + 1.02(z/L_y)^2], \quad z < L_y.$$
(6)

The parameter L_y describing the maximum escape depth of the electrons can be written in fractions of the Bethe radius r_B which determines the distance at which an electron loses all its energy without taking account of curvature of its trajectories. It was shown that for iron $L_y = 0.55 \, r_B$. However, until now the problem of a possible generalization of this expression for other substances has remained unsolved.

The analysis carried out by the authors of this paper together with Liljequist showed that a formula, true for a wide range of substances and initial electron energies, can also be proposed for L_y;

$$L_y = 780E^2/\rho \ln(E/E_0)(\text{Å}),$$
(7)

where E is the initial electron energy in keV, ρ is the density of the substance in g cm^{-3}, $E_0 = 0.39$ keV.

By means of a direct calculation using MCSM we have checked (6) and (7) for semiconductor crystals (Si, Ge, GaAs, InSb). Fig. 2 presents the results of

calculations for the probability of electron emission with energies $E = 6.18$ keV in Si for different values of z and also a curve corresponding to (6) and (7). It is seen from this figure that equation (6) for $P(z)$ agrees well with the results of the computations. An insignificant difference (less than 10%) is observed only in the case of low Z and high E and of high Z and low E, where Z is the atomic number.

The function $P(z)$ corresponds to the case where all the electrons emitted from the crystal are detected regardless of their energies (the so-called integral photoemission). The problem of finding the function $P(z)$ becomes more acute in connection with the development of a new method – depth-selective X-ray standing-wave analysis (Koval'chuk & Mukhamedzhanov, 1983, 1984; Bedzyk, Materlik & Koval'chuk, 1984) based on the detection of photo-electrons with a certain energy range ΔE. In a more general case, electrons emitted at a definite angle ψ to the surface can be selected. Then another function, $P(z, \Delta E, \Delta\psi)$, should be found instead of $P(z)$. This weight function essentially depends on what energy and angular intervals ΔE, $\Delta\psi$ are selected and what the resolution is (i.e. on the parameters of the electron spectrometer).

It should be noted that the function $P(z, \Delta E, \Delta\psi)$ can be readily found by the MCSM as an integral of the function $P(z, E, \psi)$ over the definite intervals ΔE, $\Delta\psi$, in contrast to integral functions, for finding which the integration is carried out over the entire variation range of the parameters. The function $P(z, \Delta E)$, which is integral over the energy E for three values of the energy and the angle, respectively, are shown schematically in Fig. 3.

Fig. 3. Schematic profile of the probability distribution of electron yield as a function of depth: (a) $P(z, \Delta E)$ for three energy ranges (integral over angle ψ); (b) $P(z, \Delta\cos\psi)$ for three angular intervals (integral over energy E).
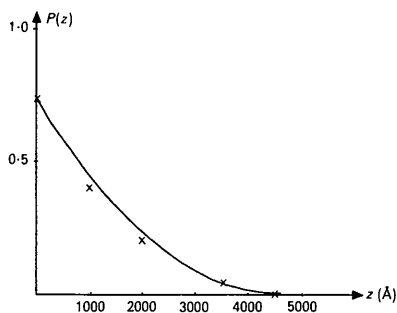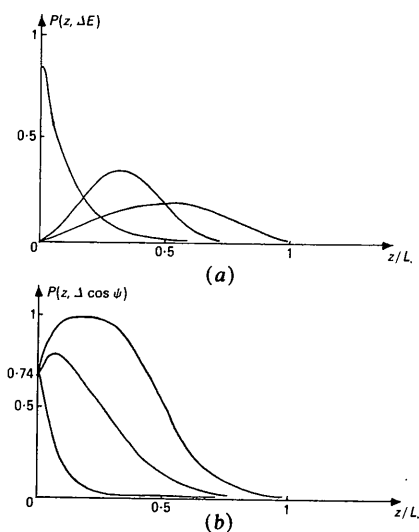

Fig. 2. Function $P(z)$ calculated from equations (6) and (7) (solid line) and Monte Carlo simulations of this function (crosses) for $E = 6.18$ keV in Si.

4. Depth-selective X-ray standing-wave analysis

Let us consider in more detail the idea of depth-selective standing-wave analysis. When an X-ray quantum has been absorbed, all the photoelectrons escaping from an atomic shell into the crystal bulk have the same energies. However, during their motion towards the surface, they lose some of their initial energy as a result of inelastic collisions. The total energy loss of the emitted electrons increases with the path within the crystal, and consequently with the depth at which an electron was generated. That is why analysing the angular dependence of the electron yield with a certain energy loss near the Bragg angle gives structural information on the layer at a certain depth.

However, the realization of this idea encounters some difficulties, primarily experimental. For instance, for the selection of electrons with certain energies a high-resolution energy analyser is needed. The higher the resolution, the fewer electrons will be detected, which in turn requires a system of storing weak signals.

At the first stage, to solve the problem of energy analysis of electrons excited by an X-ray standing wave, a low-resolution gas proportional counter was used (Koval'chuk & Mukhamedzhanov, 1983, 1984; Bedzyk, Materlik & Koval'chuk, 1984; Hertel, Koval'chuk, Afanas'ev & Imamov, 1981). For the first time photoemission curves were measured for electrons with different energy losses in Ge and Si crystals with a disturbed (or amorphous) surface layer, and a conclusion was made about the possibility of varying the effective depth of the surface layer studied (Koval'chuk & Mukhamedzhanov, 1983, 1984). To increase the sensitivity of the energy analysis by several times we have developed in our laboratory a magnetic (solenoidal) analyser (Koval'chuk & Semiletov, 1986). The selection of electrons with energies ranging between the values in question was made by choosing an appropriate value of the magnetic field in the solenoid. It should be noted that in 1975 a high-vacuum X-ray spectrometer was suggested (Kikuta, Takahashi & Tuzi, 1975). This spectrometer allowed one to select photo- and Auger electrons with different energies, based on a 127° cylindrical high-resolution electrostatical analyser. However, this device was not used for structure studies of disturbed surface layers.

The potentialities of depth-selective X-ray standing-wave analysis are clearly demonstrated in the experiment carried out using synchrotron radiation by Bedzyk, Materlik & Koval'chuk (1984). In this experiment (111) diffraction was studied from two Si single crystals, the first being a perfect crystal, the second a crystal with a disturbed (amorphous) SiO_2 film on the surface. The energy analysis of electrons was made with a gas-flow proportional counter.

Photoemission curves from an Si single crystal differ slightly only at the central part of the angular region (owing to the extinction effect). This effect allows one to calculate the average escape depth of the electrons with different energy losses (as expected, escape depth increases monotonically as electron energy losses increase). On the other hand, photoemission curves from the Si crystal with an amorphous film differ qualitatively in their shape, which clearly points to a different escape depth of the electrons with different energy losses.

5. Secondary-radiation yield under the conditions of multiple diffraction

So far, all the studies on the secondary-radiation yield under the conditions of dynamical diffraction were made in the two-wave case, where X-rays were reflected on one set of crystal planes. However, one can easily realize the case where several points of the reciprocal lattice reach the Ewald sphere simultaneously. In this case an X-ray beam is reflected from several sets of planes simultaneously, and the radiation wave field within the crystal is the sum of N plane waves (the multiple diffraction case):

$$E(\mathbf{r}, t) = \exp(-i\omega t) \sum_{m=0}^{N-1} \sum_{s=\pi,\sigma} E_{ms}(z) \exp(i\mathbf{k}_m\mathbf{r})\mathbf{e}_{ms}.$$

$$(8)$$

Here $\mathbf{e}_{ms}$ are polarization vectors, $\mathbf{k}_m = \mathbf{k}_0 + \mathbf{h}_m$, $\mathbf{h}_m$ is the reciprocal-lattice vector for the mth reflection, $\mathbf{k}_0$ is the wave vector of the incident plane wave.

If all the reciprocal-lattice vectors lie in the same plane (only this case turns out to be stable to a change of the X-ray wavelength) then the wave-field intensity is modulated not only along some direction but also in the entire plane. Under certain conditions the nodes and antinodes of the radiation field appear and form a two-dimensional lattice with periodicity copying the crystal periodicity. Consequently, additional possibilities exist for localizing the position of an impurity and determining the degree of disorder and deformation of the crystal lattice. The experimental study of the secondary-radiation yield in the multiple-diffraction case should be made using radiation monochromated and collimated in two directions. If the conventional monochromatization and collimation schemes are used, this requirement leads to great intensity losses. Thus advances in experimental studies will be connected mainly with the use of high-intensity sychrotron radiation. In such a situation greater emphasis should be laid on theory, as it should not only explain the experimental results but also determine the optimal conditions for the realization of the experiment. The basic aspects of such a theory are given below.

Let us consider a crystal with a disturbed surface layer, as before. It is convenient to introduce an

average matrix of Fourier components of crystal polarizability, depending on z:

$$\hat{\chi}_{mm'}^{(d)}(z) = \hat{\chi}_{mm'} f_{mm'}(z). \qquad (9)$$

This matrix differs from a conventional matrix $\hat{\chi}_{mm'}$ by the presence of an additional multiplier which characterizes the distortions

$$f_{mm'}(z) = \exp\left[-i\mathbf{h}_{mm'}\cdot\mathbf{u}(z) - W_{mm'}(z)\right], \qquad (10)$$

where $\mathbf{h}_{mm'} = \mathbf{k}_m - \mathbf{k}_{m'}$ are the reciprocal-lattice vectors, corresponding to an X-ray beam scattering from the direction $\mathbf{k}_m$ to the direction $\mathbf{k}_{m'}$, $W_{mm'} = \frac{1}{2}h_{mm'}^2\langle u^2\rangle$.

Amplitudes $E_{ms}(z)$ satisfy the generalized Takagi–Taupin set of equations, which can be written in the form

$$dE_{ms}/dz = (i\pi/\lambda\gamma_m)\sum_{m's'}[\chi_{mm'}^{ss'}f_{mm'} - \alpha_m\delta_{mm'}^{ss'}]E_{m's'}. \qquad (11)$$

Here $\chi_{mm'}^{ss'} = \mathbf{e}_{ms}\hat{\chi}_{mm'}\mathbf{e}_{m's'}$, λ is the X-ray wavelength, $\gamma_m = \mathbf{k}_m\mathbf{n}_0/\kappa$, $\kappa = \omega/c = 2\pi/\lambda$, $\mathbf{n}_0$ is the normal to the crystal surface, $\delta_{mm'}^{ss'}$ is the Kronecker symbol, which is equal to unity at $m = m'$ and $s = s'$ and to zero otherwise. As usual, $\chi = \chi_r + i\chi_i$ and χ_i describes the influence of inelastic scattering processes, leading to beam weakening. The parameters α_m determine the deviation from the Bragg condition for the mth reflection,

$$\alpha_m = (k_m^2 - k_0^2)/\kappa^2 = C_{m1}\Delta\theta_1 + C_{m2}\Delta\theta_2, \qquad (12)$$

where $\Delta\theta_1$, $\Delta\theta_2$ describe the difference between the direction of the incident beam and the correct multiple-diffraction direction.

The general formula (1) is true, naturally, in the case of multiple diffraction too, but now

$$\frac{dN_\nu^{(s)}(z)}{dz} = \frac{c}{8\pi}\frac{\mu_{0\nu}}{\hbar\omega}\sum_{\substack{mm'\\s's''}}\frac{\chi_{imm'}^{s's''}(\nu)}{\chi_{i0}(\nu)}$$

$$\times f_{mm'}(z)E_{ms}^{(s)}(z)E_{m's''}^{(s)}(z). \qquad (13)$$

Here and below we omit the parameters $\Delta\theta_1$, $\Delta\theta_2$ to simplify the formulae. Equations (1), (10)–(13) solve completely the problem of the theoretical calculation of the angular dependence of secondary-radiation yield from a crystal with a disturbed surface layer. These equations can also be used for the analysis of the fluorescence yield from impurity atoms localized either on the surface or in the crystal bulk. In this case χ_i of an impurity must be inserted into formula (13), instead of χ_i of the crystal bulk. Accordingly, the displacement $\mathbf{u}(z)$ and factor $W(z)$ must correspond to the impurity atoms.

These formulae are true both in the Bragg geometry and in the Laue geometry, i.e. for all signs of the parameters γ_m of the diffracted beams, which characterize their direction with respect to the crystal surface. As an example, let us consider below the prob-

lem of a direct observation of the enhanced Borrmann effect in multiple Laue diffraction in a single crystal. As shown previously by Joko & Fukuhara (1967) [see also the paper by Afanas'ev and Kohn (1977)], in symmetrical four-wave and six-wave cases the minimum absorption coefficient of X-rays is lower than in the two-beam case. This effect occurs in the narrow-angle region near the direction of accurate multiple diffraction. For this observation the photoelectron yield from the exit surface of a crystal must be registered.

The solution of the set of equations (11) in a perfect crystal can be written as a sum of exponents $B_{ms}\exp\left[((i\varepsilon_j - \mu_j)z/2]/\gamma_m^{1/2}\right]$, where $\varepsilon_j + i\mu_j$ is a complex eigenvalue of the multiple diffraction matrix

$$\sum_{m's'}G_{mm'}^{ss'}B_{m's'}(j) = (\varepsilon_j + i\mu_j)B_{ms}(j). \qquad (14)$$

It follows from (11) that the matrix G has the form

$$G_{mm'}^{ss'} = \frac{\kappa}{\gamma_m^{1/2}\gamma_{m'}^{1/2}}(\chi_{rmm'}^{ss'} - \alpha_m\delta_{mm'}^{ss'} + i\chi_{imm'}^{ss'}). \qquad (15)$$

In the case of photoelectron yield $\mu_y \gg \mu_j$, μ_0/γ_0 and the form of the function $P(z)$ is not essential. For simplicity, it is convenient to use the exponential form $P(z) = \exp\left[-\mu_y(t-z)\right]$. Then the integral (1) can be calculated analytically. The results of calculation have two terms. The first term contributes to the photoelectron yield from different sheets of the dispersion surface independently, and the second term corresponds to the interference between different sheets. If the crystal thickness t is large enough so that $t \gg L_{ex}$, then the second term is strongly oscillating as the angles $\Delta\theta_1$, $\Delta\theta_2$ change. If we average the results over the oscillation period we find that the second term equals zero and the first one does not change. Normalizing the photoelectron yield by its value in the non-diffraction regime from the entrance surface, we obtain the following formula:

$$\kappa^{(s)} = \frac{\gamma_0}{\mu_0}\sum_j\mu_j\exp\left(-\mu_j t\right)|B_{0s}(j)|^2. \qquad (16)$$

From (16) the photoelectron yield in the Laue anomalous transmission case is determined by the sum of the contributions from all sheets of the dispersion surface. The explicit value of the contribution from each sheet is proportional to the degree of excitation of the sheet on the crystal entrance surface, its absorption in the crystal bulk and the degree of interaction of the corresponding standing wave with the crystal atom. The parameter μ_y in this case does not influence the result.

We have computed the curves $\kappa^{(s)}(\Delta\theta_1)$ for different values of $\Delta\theta_2$ according to (12)–(16) in the case of four-wave ($220/400/\bar{2}20$) diffraction of Cu $K\alpha$ radiation in Si crystals. The curves are shown in Fig. 4. The surface of a crystal is perpendicular to (001), $t = 0.8$ mm. The angular deviations are chosen so that

$\Delta\theta_1$ is the deviation from the Bragg angle in the diffraction plane for the 400 reflection, while $\Delta\theta_2$ is the azimuth angle for the reflection. The choice of polarizations (π and σ) also corresponds to the two-beam (400) case.

It is clearly seen in Fig. 4 that the curve with $\Delta\theta_2 = 0$ has a dip in the region of $\Delta\theta_1$ values near zero, which is due to the enhanced Borrmann effect. The absence of the peak corresponding to 400 diffraction in the case of π-polarized radiation at greater values of azimuth is because the Borrmann effect for π-polarized radiation is weakly manifested and the radiation is absorbed to a large extent. The reason lies in the small value of the polarization factor. For both 220 and $\bar{2}20$ reflections the polarization is mixed (neither π nor σ). Equation (16) is also true, naturally, for the two-wave diffraction; besides, the two-wave peaks are also shown in Fig. 4 for greater values of the azimuth $\Delta\theta_2$. In this case the dip on the curves is hardly seen, which is caused by the fact that the dependence of μ on the angle $\Delta\theta_1$ in the two-wave case is more even.

The analysis of the angular dependence of the photoemission and fluorescence yield in multiple diffraction can provide, in our opinion, interesting information on the crystal structure and the character of interaction of X-rays with the substance. In fact, this is a new and promising direction of investigation which is awaiting development. The potentialities of this method exceed by far the example given in this section.

6. Concluding remarks

The new direction in dynamical diffraction studies which has recently appeared in connection with the detection of the photoelectron yield excited by an X-ray standing wave provides immensely important information on the structure of subsurface crystal layers. In contrast to fluorescence, which determines the position of an impurity atom or absorbed atoms in the crystal lattice, the photoelectron yield allows one to determine the distortions of the crystal bulk itself, under different external influences.

It should be noted here that, besides the photoelectron yield considered in this paper, we are developing another direction in the studies carried out in our laboratory, which is concerned with the investigation of the photoelectron voltage excited by an X-ray standing wave [see Zheludeva, Koval'chuk & Kohn (1985) and references therein]. During the detection of this secondary process the angular dependence of the photoelectric voltage in a perfect semiconductor crystal with p-n transition is measured. A striking characteristic of this secondary process is the fact that in this case the behaviour of the angular dependence is accounted for not only by an X-ray wave field but also by some electrophysical parameters (diffusion lengths of minority carriers in p and n regions).

It should also be noted that the use of synchrotron radiation (SR) opens up wide prospects for the investigation of secondary processes under dynamical diffraction conditions. The high intensity of SR permits the realization of unique experiments under the conditions of both conventional two-wave diffraction and multiple diffraction.

Thus, the recent 20 years have meant a new life for the theory of X-ray dynamical diffraction developed by P. P. Ewald. The registration of secondary radiation has become the basis for the development of a new method of structure studies of subsurface layers in single crystals.
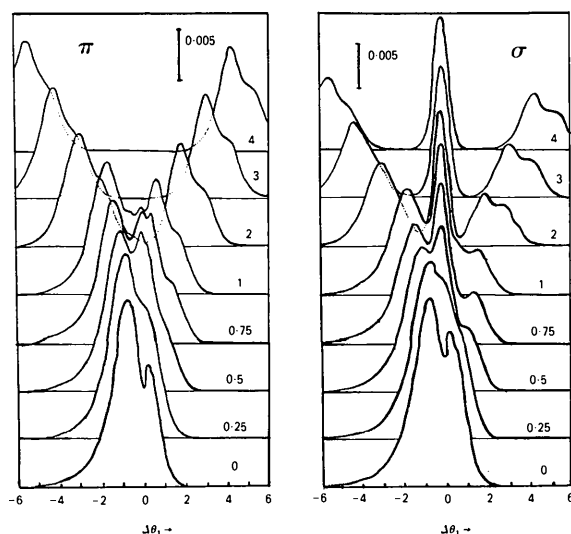

Fig. 4. Theoretical curves of photoemission angular dependence $\kappa^{(s)}(\Delta\theta_1)$ at different values of $\Delta\theta_2$ for the case of four-wave $(200/400/\bar{2}20)$ diffraction of Cu $K\alpha$ radiation in Si. Angles $\Delta\theta_1$, $\Delta\theta_2$ measured in 10^{-5} rad. $\Delta\theta_2$ values are denoted on the curves, the maximum yield ~ 0.02.

References

AFANAS'EV, A. M. & KOHN, V. G. (1977). Acta Cryst. A33, 178-184.
AFANAS'EV, A. M. & KOHN, V. G. (1978). Zh. Eksp. Teor. Fiz. 74, 300-313.
BATTERMAN, B. W. (1962). Appl. Phys. Lett. 1, 68-69.
BEDZYK, M. J., MATERLIK, G. & KOVAL'CHUK, M. V. (1984). Phys. Rev. B, 30, 4881-4884.
BURGEAT, J. & TAUPIN, D. (1968). Acta Cryst. A24, 99-102.
HERTEL, N., KOVAL'CHUK, M. V., AFANAS'EV, A. M. & IMAMOV, R. M. (1981). Phys. Lett. A, 75, 501-502.
JOKO, T. & FUKUHARA, A. (1967). J. Phys. Soc. Jpn, 22, 597-604.
KIKUTA, S., TAKAHASHI, T. & TUZI, Y. (1975). Phys. Lett. A, 50, 453-454.
KOHN, V. G. & KOVAL'CHUK, M. V. (1981). Phys. Status Solidi A, 64, 359-366.
KOVAL'CHUK, M. V. & KOHN, V. G. (1986). Usp. Fiz. Nauk, 149, 69-103.
KOVAL'CHUK, M. V., KOHN, V. G. & LOBANOVICH, E. F. (1985). Fiz. Tverd. Tela, 27, 3379-3387.

KOVAL'CHUK, M. V. & MUKHAMEDZHANOV, E. KH. (1983). *Fiz. Tverd. Tela*, **25**, 3532-3536.

KOVAL'CHUK, M. V. & MUKHAMEDZHANOV E. KH. (1984). *Phys. Status Solidi A*, **81**, 427-432.

KOVAL'CHUK, M. V. & SEMILETOV, A. S. (1986). *Fiz. Tverd. Tela*, **28**, 558-561.

LILJEQUIST, D. (1979). *Electron Penetration in Solids and its Applications to Mössbauer Spectroscopy.* Preprint. Univ. Stockholm.

SHCHEMELEV, V. N., EFIMOV, O. N. & KRUGLOV, M. V. (1974). *Uch. Zap. Leningr. Gos. Univ.* **370**, 83-87.

SHCHEMELEV, V. N. & KRUGLOV, M. V. (1972). *Fiz. Tverd. Tela*, **14**, 3556-3562.

SHCHEMELEV, V. N. & KRUGLOV, M. V. (1975). *Fiz. Tverd. Tela*, **17**, 403-408.

SHCHEMELEV, V. N., KRUGLOV, M. V. & PRONIN, V. P. (1970). *Fiz. Tverd. Tela*, **12**, 2495-2497.

SOZONTOV, E. A., KRUGLOV, M. V. & ZAKHAROV, B. G. (1979). *Elektron. Tekh. Ser. 6: Mater.* 7(132), 108-113.

SOZONTOV, E. A., KRUGLOV, M. V. & ZAKHAROV, B. G. (1981). *Phys. Status Solidi A*, **66**, 303-310.

ZHELUDEVA, S. I., KOVAL'CHUK, M. V. & KOHN, V. G. (1985). *J. Phys. C*, **18**, 2287-2304.

Low-Symmetric Coordination Polyhedra – Pseudosymmetry and Idealization

BY H. LUEKEN* AND U. ELSENHANS

Institut für Anorganische Chemie der Technischen Universität Clausthal,
D-3392 Clausthal-Zellerfeld, Federal Republic of Germany

AND U. STAMM

Institut für Anorganische Chemie der Technischen Hochschule Aachen, D-5100 Aachen,
Federal Republic of Germany

Abstract

A method is described for the analysis of symmetryless or low-symmetric coordination polyhedra with respect to their pseudosymmetry, regardless of coordination number. With lattice sums of spherical harmonics, symmetry-adapted orientations of the real polyhedra in the various point groups are ascertained by fitting procedures. The idealized polyhedra can then be constructed by averaging and optimizing the positional parameters of those atoms which are symmetry equivalent in the idealized arrangements. The degree of distortion of the real polyhedra with regard to the idealized polyhedra is specified by the mean value of relative atom displacements. The method can assist in the investigation of factors affecting crystal structure and in the interpretation of spectroscopic and magnetic properties of compounds with d and f elements. The analysis is applied to $LiCeO_2$ where a symmetryless arrangement of the O atoms around the Ce atom occurs with coordination number seven.

1. Introduction

In the discussion of crystal structures the description of the existing coordination polyhedra (CP) and their

comparison with known ideal arrangements are of great importance (Wells, 1984). The investigation of the relationship between real, *i.e.* normally distorted, polyhedra and ideal polyhedra can be useful in various ways such as the ascertainment of factors affecting crystal structure. In the case of complexes the shape of the CP will depend on the chemical bonding between the central atom and the ligands, on mutual repulsions of the ligands, and on the packing relations in the crystal structure (Hoard & Silverton, 1963). The consequences of these influences are in most cases distortions relative to those polyhedron models that are predicted, for example, from the pure electrostatic point of view (point charges) or from the packing of rigid spheres. In intermetallic compounds deviations from Laves principles (Laves, 1956) can occur if covalent bonds, *i.e.* bonds with directional character, exist (Pearson, 1972). Idealizations of low-symmetric arrangements with a special pseudosymmetry also facilitate the investigation of spectroscopic and magnetic properties of transition-metal and rare-earth compounds. Raising the symmetry normally leads to a drastic decrease of the number of crystal-field parameters and therefore reduces the problem.

The description and idealization of low-symmetric CP can be complicated by a high degree of distortion, by an unsuitable orientation of the CP to the cell edges and/or by high coordination numbers (CN).

---

* Present address: Institut für Anorganische Chemie der Technischen Hochschule Aachen, D-5100 Aachen, Federal Republic of Germany.