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External photoeffect in the diffraction of x rays in a crystal with a perturbed layer

A. M. Afanas'ev and V. G. Kon

I. V. Kurchatov Institute of Atomic Energy
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A general theory is constructed of the emission of secondary rays in Bragg diffraction of x rays in an ideal crystal and in a crystal with a perturbed surface layer. In the case of photoemission, the angular dependence of the photoelectron emission is extremely sensitive to weak displacements of the atoms in the surface layer. The question of the possibility of extracting information on the structure of the perturbed layer is analyzed in detail. It is shown that in a number of situations the aggregate of the data provided by the photoemission curve and the reflection curve permits a complete reconstruction of the structure of the perturbations in the surface layer, including both the averaged and random displacements of the atoms from their positions in an ideal crystal.

1. INTRODUCTION

The diffraction scattering of x rays in thick crystals of high degree of perfection, in the so-called dynamic regime, is characterized by the formation of a single wave field by coherent superposition of the incident and diffracted waves. The structure of this field, i.e., the distribution of its nodes and antinodes, depends strongly on the angle of incidence of the x rays on the crystal. This leads in turn to a strong angular dependence of the cross sections of the inelastic processes such as the photoeffect, fluorescence, Compton scattering, and others, which decrease strongly when the field nodes are at the crystal atoms, and conversely increase when the crystal lattice sites correspond to antinodes of the combined electric field. A reflection of this circumstance is the sharp decrease of the x-ray absorption coefficient in diffraction in the Laue geometry, observed by Borrmann in 1941—the so-called anomalous passage effect (see, e.g.,[11]).

The changes of the intensities of the inelastic processes can be investigated also directly, by studying the angular dependence of the emission of secondary rays. The first to choose this procedure, namely measurement of the angular dependence of the yield of the $n-\gamma$ reaction, was Knowles,[2] in an investigation of the anomalous passage of thermal neutrons in perfect calcite crystals. In the Sixties, starting with the pioneering work of Batterman,[3] extensive investigations have been made of secondary processes (fluorescence,[3-5] thermal diffuse scattering[6,7] Compton scattering[8]) that accompany the diffraction of x rays. In all cases, strongly pronounced anomalies were observed in the angular dependence of the secondary emission near the Bragg angle. However, in view of the large depths L of emergence of the secondary radiations investigated in,[3-7] which greatly exceed the extinction length L_{ex} of the x rays, the observed anomalies took mainly the form of dips on the yield curves, and only a small asymmetry of the curve reflected the structure of the wave field.

The situation changes radically if one registers the emission from the crystal of photoelectrons for which L is always much less than L_{ex}. Such investigations were first initiated in the early Seventies at the initiative of O. N. Efimov at the Leningrad University. It was shown even in the first papers[8,9] that the photoelectron yield curve reflects primarily the structure of the wave field in the crystal, while the extinction of the x rays has little effect. This circumstance was the basis of a new method of investigating structural imperfections produced in a crystal by various types of external action.[10-12]

Later on Golovchenko, Batterman, and Brown[13] found a method of decreasing the parameter L also in

the case of fluorescence emission, by introducing impurities at a small depth; this also enabled them to observe the structure of the wave field in the crystal, in full analogy with the results of [8,9]. Quite recently two groups working independently—Kruglov and Shchemelev[14] on photoemission curves, and Anderson, Golovchenko, and Mair[15] on the fluorescence yield curves from impurity atoms at small depths—have demonstrated experimentally that the methods indicated above are *extremely sensitive* to very weak distortion of the crystal structure, when *the total displacement of the crystal surface* as a result of external action (say, ion implantation) *is a small fraction of the interatomic distance*. This fact is not yet widely known; moreover, there is no detailed theoretical analysis whatever of this question.

The high sensitivity of the photoemission curves at a small depth of emergence of the photoelectrons to the total displacement of the surface layer is more or less physically obvious, and this idea was already advanced by one of us (Afans'ev) in the analysis of the data of [10]. A much more complicated and important theoretical problem is to determine how much information on the structure of the imperfect layer can be extracted from the data on the angular dependence of the photoelectron emission.

The present paper is devoted mainly to this question. It will be shown in Sec. 3 that the aggregate of the data provided by the reflection and photoemission curves can permit, for an entire class of imperfections, the reconstruction of the structure of the distortions of the crystal lattice over the entire surface layer. In Sec. 2 we obtain general formulas that describe the angular dependence of the emission of the secondary rays, and consider the case of an ideal crystal.

2. FORMULATION OF PROBLEM AND DERIVATION OF GENERAL FORMULAS

Assume that x rays are incident on a crystal that is made slightly imperfect by some external action. Let the incidence angle be close to the Bragg angle and let the diffracted wave emerge from the irradiated (entrance) surface of the crystal (the so-called Bragg-geometry diffraction). We assume that the imperfections are uniform along the surface, i.e., the parameters of the perturbed layer depend only on the coordinate z, which is the distance to the entrance surface of the crystal. The imperfections in the crystal will be described by two parameters: the displacement $u(z)$ of the atomic planes from positions corresponding to the ideal crystal, and by the static Debye-Waller factor $e^{-W(z)}$, which takes into account the random displacements of the atoms from the positions corresponding to the average displacements.

The electric-field vector of the x-ray wave in such a crystal is given by

$$E(\mathbf{r}) = E_0(z) \exp(i\mathbf{k}_0\mathbf{r}) + E_h(z) \exp(i\mathbf{k}_h\mathbf{r}), \tag{1}$$

where $\mathbf{k}_0$ and $\mathbf{k}_h$ are the wave vectors in the directions

of the incident and diffracted waves, respectively. For the amplitudes $E_0(z)$ and $E_h(z)$ we readily obtain directly from Maxwell's equations the following system of equations, first proposed by Takagi[16]:

$$\frac{dE_0^i}{dz} = \frac{ik}{2\gamma_0}[\chi_0^{il}E_0^l + \chi_h^{il}e^{i\varphi(z)-W(z)}E_h^l],$$

$$\frac{dE_h^i}{dz} = -\frac{ik}{2|\gamma_h|}[(\chi_0^{il} - \alpha\delta^{il})E_h^l + \chi_{\bar h}^{il}e^{-i\varphi(z)-W(z)}E_0^l]. \tag{2}$$

Summation over repeated indices is implied throughout, $k = \omega/c$, $\varphi(z) = \mathbf{h}\cdot\mathbf{u}(z)$, $\mathbf{h}$ and $\bar{\mathbf{h}} = -\mathbf{h}$ are the reciprocal-lattice vector multiplied by 2π, $\gamma_{0,h}$ are the cosines of the angles between the vectors $\mathbf{k}_{0,h}$ and the inward normal to the entrance plane of the crystal. The parameter α determines the deviation from the Bragg condition.

The Fourier components of the polarizability tensor $\chi_{0,h}$ can be represented in the form

$$\chi_{0,h} = \chi_{r0,h} + i\chi_{i0,h},$$

where $\chi_{r0,h}$ and $\chi_{i0,h}$ are proportional to the real and imaginary parts of the amplitude of the scattering by the unit cell of the crystal, respectively. As a result of the optical theorem, χ_{i0} is linearly connected with the total x-ray absorption coefficient μ_0. A variety of processes contribute to the x-ray absorption: the photoeffect (PH), thermal diffuse scattering (TDS), and Compton scattering (CS). Accordingly, χ_i can be represented as a sum of terms, each of which describes a definite absorption process:

$$\chi_i = \chi_i(PH) + \chi_i(TDS) + \chi_i(CS). \tag{3}$$

To find the intensity of the secondary emissions, we consider a layer located at a depth z and having a thickness dz. The total x-ray absorption in this layer is obviously determined by the difference between the incoming and outgoing fluxes, i.e.,

$$\varkappa(z)dz = \gamma_0(|E_0(z)|^2 - |E_0(z+dz)|^2) + |\gamma_h|(|E_h(z+dz)|^2 - |E_h(z)|^2)$$

$$= \left(-\gamma_0\frac{d|E_0(z)|^2}{dz} + |\gamma_h|\frac{d|E_h(z)|^2}{dz}\right)dz.$$

Using (2), we readily obtain

$$\varkappa(z) = k[E_0^{i*}(z)\chi_{i0}^{il}E_0^l(z) + E_h^{i*}(z)\chi_{i0}^{il}E_h^l(z)]$$
$$+ 2k\operatorname{Re}[E_0^{i*}(z)\chi_{i\bar h}^{il}E_h^l(z)e^{i\varphi(z)-W(z)}]. \tag{4}$$

With the aid of (3) we can easily separate the contribution made to the absorption by any of these processes. To this end it is obviously necessary to replace χ_i in (4) by $\chi_i(A)$—the quantity corresponding to the process of interest to us. If the probability of the secondary emission from the crystal is given by the function $P_A(z)$, then the registered intensity is determined as follows:

$$\varkappa_A(\alpha) = \int_0^\infty dz\, P_A(z)\varkappa_A(z,\alpha), \tag{5}$$

$$\varkappa_A(z,\alpha) = k[E_0^{i*}(z,\alpha)\chi_{i0}^{il}(A)E_0^l(z,\alpha) + E_h^{i*}(z,\alpha)\chi_{i0}^{il}(A)E_h^l(z,\alpha)]$$
$$+ 2k\operatorname{Re}[E_0^{i*}(z,\alpha)\chi_{i\bar h}^{il}(A)E_h^l(z,\alpha)e^{i\varphi(z)-W(z)}].$$

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We have introduced here explicitly the dependence on the angle of incidence of the x rays in the crystal, a dependence already contained in Eqs. (2) and (4) above, via the parameter α.

Formula (5) provides in fact the complete solution of the problem of the angular dependence of the secondary emission. Specific features of any particular process are expressed via the coefficients $\chi_{i0,h}(A)$ and the function $P_A(z)$. The amplitudes $\mathbf{E}_0(z,\alpha)$ and $\mathbf{E}_h(z,\alpha)$, naturally, do not depend on the type of the registered secondary radiation and are determined only by the diffraction-scattering process. If the crystal-lattice distortion is known, i.e., if the functions $\varphi(z)$ and $W(z)$ are given, then the amplitudes $\mathbf{E}_{0,h}(z,\alpha)$ can be obtained, for example, by numerically solving Eqs. (2) with the corresponding boundary conditions. We note that since Eqs. (2) contain the complete polarizability tensor, it suffices to retain in their solutions only the principal contributions to χ, i.e., the Thomson scattering and the dipole part of the photoelectric absorption. If only these processes are taken into account, the polarizability is a scalar: $\chi_{0,h}^{il} = \chi_{0,h}\delta^{il}$. In this case, as usual, we can introduce the unit vectors of the standard polarizations $\pi_{0,h}$ and σ.[1] For simplicity we shall assume below that the radiation incident on the crystal is σ-polarized.

In the case of an ideal crystal ($\varphi(z) = W(z) = 0$), the field distribution is well known:

$$\mathbf{E}_{0,h}(z,\alpha) = \sigma E_{0,h}(0,\alpha)\exp[ik\varepsilon(\alpha)z/\gamma_0],$$
$$E_0(0,\alpha) = E_{in}, \quad E_h(0,\alpha) = \sqrt{\beta}R_0(\alpha)E_{in}. \tag{6}$$

Here E_{in} is the amplitude of the wave incident on the crystal,

$$\varepsilon(\alpha) = \tfrac{1}{2}\{\chi_0 + \sqrt{\beta}\sqrt{\chi_h\chi_{\bar{h}}}(y \pm \sqrt{y^2-1})\}, \tag{7}$$
$$R_0(\alpha) = \sqrt{\chi_h/\chi_{\bar{h}}}(y \pm \sqrt{y^2-1}), \tag{8}$$
$$y = [\alpha\beta - \chi_0(1+\beta)]/2\sqrt{\beta}\sqrt{\chi_h\chi_{\bar{h}}}, \quad \beta = \gamma_0/|\gamma_h|. \tag{9}$$

The sign in front of the square root in (7) and (8) is determined by the condition $\mathrm{Im}\,\varepsilon(\alpha) > 0$.

Substituting (6) in (5), we obtain

$$\varkappa_A^{id}(\alpha) = |E_{in}|^2\mu_0(A)\{1 + \beta P_R(\alpha) + 2\sqrt{\beta}\,\mathrm{Re}\,(e_{\bar{h}}(A)R_0(\alpha))\}\int_0^\infty dz\,P_A(z)e^{-\mu(\alpha)z}, \tag{10}$$

where

$$\mu_0(A) = k\sigma'\sigma'\chi_{i0}^{il}(A), \quad e_{\bar{h}}(A) = k\sigma'\sigma'\chi_{i\bar{h}}^{il}(A)/\mu_0(A),$$
$$\mu(\alpha) = 2(k/\gamma_0)\,\mathrm{Im}\,\varepsilon(\alpha), \quad P_R = |R_0|^2. \tag{11}$$

The quantity $\mu(\alpha)$ is called the interference damping coefficient, and P_R is the reflection coefficient.

Formula (10) solves the problem of the angular dependence of the secondary emission from an ideal crystal and can be used for any of the secondary processes—photoeffect, fluorescence, thermal diffuse scattering, and others. A separate analysis of the specifics of each of the processes is outside the scope of the present paper. We shall dwell here only on the most significant and rather general consequences of (10), and make the following preliminary remark. Assume that the parameter $e_{\bar{h}}(A)$ in (10) coincides with the corresponding one in Eqs. (2), i.e.,

$$e_{\bar{h}}(A) = \chi_{\bar{h}}/\chi_{i0}. \tag{12}$$

As noted above, $\chi_{i0,h}$ is determined by the dipole part of the photoelectric absorption, so that condition (12) can be regarded as satisfied, with a certain degree of accuracy, for photoemission and fluoresence from the atoms of the main matrix of the crystal.

In this case, using formulas (7)–(9) and (11), we can easily transform the expression in the curly brackets of (10) into $(1 - P_R(\alpha))\mu(\alpha)$. Formula (10) then becomes

$$\varkappa_A^{id}(\alpha) = |E_{in}|^2\mu_0(A)(1-P_R(\alpha))\mu(\alpha)\int_0^\infty dz\,P_A(z)e^{-\mu(\alpha)z}. \tag{13}$$

A formula of this type was derived in[3] and then used to analyze the experimental data in a number of succeeding studies. It is clear from the foregoing, however, that the region of applicability of this formula is limited, and it cannot be used for such processes as thermal diffusion scattering and Compton scattering, or fluoresecence from impurities, where condition (12) is certainly not satisfied.

We note that even in the case of the photoeffect the use of formula (13) is not fully correct. Indeed, the photoeffect gives rise to various groups of electrons that correspond to transitions from different atomic shells. Each such group has its own emergence length L_A, and also its own parameter $e_{\bar{h}}(A)$, since the value of $e_{\bar{h}}$ varies with the electron shell from which the electron is detached (see, e.g.,[17]). Formula (10) should therefore be used also in the case of photoelectric absorption separately for the different electron groups, and only then should the contributions from all the groups be summed.

Thus, although no qualitative differences is observed in this case between the yield curves obtained with formulas (13) and (10), formula (10) is nevertheless preferable, since it is exact, while (13) is approximate.

We consider now the behavior of the interference damping coefficient $\mu(\alpha)$. Far from the bragg angle ($|y| \gg 1$) we have $\mu(\alpha) = \mu_0/\gamma_0$, and in the region ($|y| \leqslant 1$) of total reflection $\mu(\alpha)$ increases sharply to a value $\mu_{ex} = 2/L_{ex}$, where L_{ex} is the extinction length and is determined by the relation

$$L_{ex} = 2\sqrt{\gamma_0|\gamma_h|}/k|\chi_{rh}|. \tag{14}$$

A typical behavior of $\mu(\alpha)$ is shown in Fig. 1.

It is easily seen from (10), the character of the angular dependence $\varkappa(\alpha)$ will be determined to a substantial degree by the value of the average depth of emergence of the secondary emission L, or more accurately by the ratio of L and L_{ex}. By way of example we consider the limiting cases. At $L \gg L_{ex}$ it is convenient to investigate formula (13). In this case the function $P_A(z)$, which varies slowly in comparison with the exponential factor,
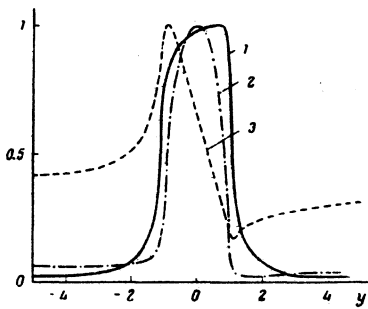
FIG. 1. Angular dependence of the x-ray reflection coefficient $P_R(y)/P_{R\ max}$ (curve 1), of the damping coefficient $\mu(y)/\mu_{max}$ (curve 2), and the photoelectron emission $\varkappa^{id}(y)/\varkappa^{id}_{max}$ (curve 3 for an ideal silicon crystal in the case of (111) reflection of the Cu $K\alpha$ line: $P_{R\ max} = 0.937$, $\mu_{max} = 22.1\ \mu_0/\gamma_0$, and $\varkappa^{id}_{max} = 2.80$ $\varkappa^{id}(\infty)$.

can be replaced by its value at $z = 0$. As a result we get for $\varkappa(\alpha)$, apart from inessential constant factors,

$$\varkappa^{id}(\alpha)_{L\to\infty} = 1 - P_R(\varkappa). \tag{15}$$

In the opposite limiting case $L \ll L_{ex}$ we can replace $e^{-\mu(\alpha)\varkappa}$ in (10) by unity. Then

$$\varkappa^{id}(\alpha)_{L\to 0} = \{1 + \beta P_R(\alpha) + 2\sqrt{\beta}\ \mathrm{Re}\ (e_{\bar{h}}R_e(\alpha))\}. \tag{16}$$

It follows from (15) that at $L \gg L_{ex}$ the secondary-emission curve is simply the inverted reflection curve, i.e., by measuring $\varkappa(\alpha)$ we can determine in this case accurately the angular position of the Bragg reflection, but this does in fact yield no new information on the diffraction scattering, compared with the information contained in the reflection curve $P_R(\alpha)$. Actually, allowance for the fact that L is finite leads to corrections of the order of L_{ex}/L in formula (15), and these already contain information on the structure of the wave field at the investigated crystal atoms, i.e., those which serve as sources of secondary radiation.

We shall not stop here to analyze this question, which has already been discussed in sufficient detail in [3]. We note only that the use of radiation of this type with $L \ll L_{ex}$ (meaning all the types of radiation except photoemission), in view of the just mentioned distinctions between them, can hardly be of any use for the investigation of the structure of the imperfect crystal.

The situation is radically altered in the opposite case $L \ll L_{ex}$. This is precisely the situation typical of photoemission. Indeed, in this case the $\varkappa(\alpha)$ curve differs strongly from the reflection curve and offers a direct representation of the summary wave field at the atomic planes. If we disregard the inessential angular dependence of the cross section for photoabsorption by individual atoms, then formula (16) with allowance for (6) can be represented in the form

$$\varkappa^{id}(\alpha)_{L\to 0} \approx \sum_{\text{cell}} |E_0(0, \alpha) + E_h(0, \alpha)e^{ihr}|^2.$$

It is most important here that within the limits of the total-reflection region ($|y| \leqslant 1$) the modulus of the field $E_h(0, \alpha)$ remains practically unchanged, but its phase changes greatly, from zero to π. This behavior can be

readily seen from formulas (6), (8), and (9). Typical curves for $\varkappa^{id}_{L=0}(\alpha)$ and $P_R(\alpha)$ are shown in Fig. 1. A clearly pronounced interference pattern in the photoemission curve was first established experimentally in [8,9].

It should be noted that similar results can be obtained also by investigating the fluorescence from impurity atoms implanted in a surface layer of a crystal. Formula (10) is no longer suitable for the description of this case, and must be modified. First, the function $P_A(z)$ must be replaced by $c_{im}(z)P_Z(z)$, where $c_{im}(z)$ is the concentration of the impurity as a function of the depth of the implantation. In addition, it is necessary to replace χ_{i0} and χ_{ih} by $\chi^{(im)}_{i0}$ and $\chi^{(im)}_{ih}$, which leads to a renormalization of the quantities $\mu_0(A)$ and $e_{\bar{h}}(A)$ in accordance with formula (11). It is quite important here that, depending on the location of the impurity in the unit cell (ρ_{im}), an additional phase factor appears $\exp(ih \cdot \rho_{im})$, and can radically alter the form of the $\varkappa(\alpha)$ curve. As a result we have

$$\varkappa^{(im)}(\alpha) = |E_{in}|^2 \mu^{(im)}_0 \{1 + \beta P_R(\alpha)$$
$$+ 2\sqrt{\beta}\ \mathrm{Re}[e^{(im)}_h R_0(\varkappa)\exp(ih\rho_{im})]\} \int_0^{\infty} dz\, c_{im}(z)P(z)e^{-\mu(\alpha)z}. \tag{17}$$

If the depth of the impurities is $L_{im} \ll L_{ex}$ and $\rho_{im} = 0$, then we again obtain a formula close to (16). Curves of similar type were obtained in [13], where fluorescence of arsenic implanted in silicon was investigated.

3. PHOTOEMISSION FROM CRYSTALS WITH IMPERFECT SURFACE LAYERS

As noted above, Eqs. (5) and (2) solve completely the problem of finding the angular dependence of the secondary emission, provided that the distortions of the crystal lattice are known. This raises, however, a much more important problem, namely the determination of the lattice distortions from the experimentally obtained angular dependence $\varkappa(\alpha)$. In this problem, too, the photoemission method provides offers exceptionally great opportunities, in view of the small depth from which the photoelectrons are emitted. This can be seen already directly from formula (5). Indeed, consider the limiting situation, when the emission depth is so small that the changes of the fields $E_{0,h}(z)$ and of the distortions of the crystal lattice ($\varphi(z)$ and $W(z)$) can be completely neglected over distances on the order of L. In this case we obtain for $\varkappa(y)$

$$\varkappa(y) = 1 + \beta|R(y)|^2 + 2\sqrt{\beta}\ \mathrm{Re}\,(e_{\bar{h}}R(y)e^{i\varphi(0)-W(0)}), \tag{18}$$

where

$$R(y) = E_h(0, y)/\sqrt{\beta}E_0(0, y)$$

is the amplitude of the reflection of the x rays by the crystal, including the reflection by the perturbed layer. We have left out of (18) all the inessential constant factors. Moreover, we shall use henceforth the parameter y, or more accurately its real part, as the angle variable.

Assume that the perturbations extend over a layer

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whose thickness L_{per} is small compared with the extinction length. With allowance for the approximations already made, the case in question is determined by the inequalities

$$L \ll L_{per} \ll L_{ex}. \tag{19}$$

We confine ourselves below to an analysis of only this situation. It is clear that when condition (19) is satisfied, the increment made to the amplitude $R(y)$ on account of reflection in the layer is small compared with unity. From (2) it is easy to find that, accurate to terms quadratic in the parameter $l_{per} = L_{per}/L_{ex}$, we have

$$R(y) = R_0(y) + \Delta R(y), \tag{20}$$

$$\Delta R(y) = i \frac{\chi_h}{|\chi_{rh}|} \int_0^{l_m} dz \, e^{-2iyz} (e^{-i\varphi(z) - W(z)} - 1)$$

$$+ i \frac{\chi_{\bar{h}}}{|\chi_{rh}|} R_0^2(y) \int_0^{l_m} dz \, e^{-2iyz} (e^{i\varphi(z) - W(z)} - 1). \tag{21}$$

In (21) and everywhere below the coordinate z is reckoned in extinction lengths.

We consider first the angle region $|y| < 1$, where $|R_0(y)| \sim 1$, and neglect in (20) the correction for the scattering by the imperfect layer, i.e., we replace $R(y)$ by $R_0(y)$. The distortions of the crystal lattice in the imperfect layer manifest themselves on the $\varkappa(y)$ curve via the factor $W(0)$ and the phase

$$\varphi(0) = hu(0), \tag{22}$$

which is determined by the displacement $u(0)$ of the crystal surface. It is clear that the change of the phase by an amount on the order of unity should lead to a sharp change of the form of $\varkappa(y)$. Figure 2 shows plots of $\varkappa(y)$ calculated from formula (18), in which $R(y)$ is replaced by $R_0(y)$, at different values of the phase $\varphi(0)$. We note that, for example, the phase $\varphi(0) = \pi/2$ for the (333) reflection from a diamond-type lattice corresponds to a surface displacement of only $\sim a/20$, where a is the lattice constant. On the other hand, $\varkappa(y)$ curves with $\varphi = \pi/2$ and $\varphi = 0$ differ very greatly, and in fact substantially smaller changes of the phase are noticeably discernible on the $\varkappa(y)$ curves. This example demonstrates the degree of sensitivity of the photoemission yield curves to perturbations of the crystal structure of the surface layer.

The high sensitivity of the photoelectron emission yield curves to the total displacement of the surface of a crystal with a perturbed layer was clearly demonstrated by the experiments of Kruglov and Shchemelev,[14] who measured the angular dependence of the photoemission from a silicon crystal in which boron ions were implanted. They used the low energy K_α line of Ca to ensure satisfaction of the inequality (19). Etching layer after layer of the perturbed surface produced a series of curves corresponding to different values of the phase $\varphi(0)$, from $3\pi/4$ to zero.

Independently and somewhat later, similar results were obtained by Andersen, Golovchenko, and Mair in an investigation of the fluorescence of an arsenic impurity in silicon following implantation of nitrogen ions. Since the arsenic did not penetrate deeply, the
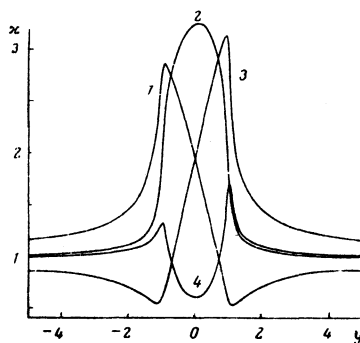

FIG. 2. Angular dependence of the photoelectron yield, calculated from formula (18) in the approximation $R(y) = R_0(y)$ and $W(0) = 0$, for different values of the phase $\varphi(0) = 0$ (curve 1), $\pi/2$ (curve 2), π (curve 3), and $3\pi/2$ (curve 4). The calculation was made for silicon, the Cu K_α line, and the (111) reflection of the x-ray lines.

perturbed layer was produced mainly by the nitrogen ions. By varying the irradiation dose and the energy of the nitrogen ions, Andersen et al. also obtained a series of curves corresponding to different values of the phase (0).

The physical cause of the high sensitivity to the surface displacement is the following. The amplitude of the refracted wave $E_0(z, y)$ near the surface ($z = 0$) differs little from E_{in}, a fact that follows directly from the E_{in} boundary conditions. As to the amplitude $E_h(z, y)$ of the reflected wave near the surface, it depends on the thickness of the entire crystal together with the substrate. If the substrate thickness is much large than L_{ex}, the amplitudes E_h and E_0 in the angle region $|y| < 1$ are comparable in magnitude, and in this case the field of the x-ray wave acquires a clearly pronounced periodicity in the direction of the vector h, and the period is smaller by an integer factor than the crystal lattice parameter, or else is equal to the latter. Owing to the weakness of the interaction of the x rays with the crystal atoms, this field structure, once produced in the substrate, is preserved also in the perturbed layer provided that $L_{per} \ll L_{ex}$. The shift of the surface by an amount smaller than the lattice parameter is precisely the indication of this periodicity of the x-ray field.

This can be observed, however, only when a large number of the atoms—the sources of the secondary radiation—preserve distinct phase relationships, i.e., when some long-range order exists on the surface. On the other hand it is obvious that the defects in the perturbed layer lead to a certain disorder in the arrangement of the atoms near the defect. Different atoms land in different positions of the "unit cell" of the x-ray field, and this leads to a smearing of the phase relationships, and after averaging over a region near the defect—to an extinction of the interference term. Allowance for the short-range disorder is the task of the static Debye-Waller factor $e^{-W(0)}$. For a layer that has been made completely amorphous $e^{-W(0)} \to 0$ and the interference term drops out completely. We note that in this case the $\varkappa(y)$ curve contains new information compared with the reflection curve, since x-ray reflection is insensitive to the presence of an amorphous layer on the crystal surface.

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We see thus that it is possible to extract directly from the $\varkappa(v)$ curves such data on the structure of the perturbed layer as the total displacement of the crystal surface or the degree of amorphization of the structure on the surface. In fact, there are many more extensive possibilities of obtaining information from photoemission data.

Indeed, the quantities $\varphi(0)$ and $W(0)$ are determined from the character of the $\varkappa(y)$ curve in the narrow angle region $|y| < 1$. However the $\varkappa(y)$ curve has, as a rule, also weak contracted "tails" due to scattering by the perturbed layer. In this range of angles, the square of the ratio $E_h(z)/E_0(z)$ can be neglected in the entire crystal and as a result we get for $R(y)$ the formula

$$R(y) = i\frac{\chi_h}{|\chi_{rh}|}\int_0^\infty dz\, e^{-2iyz}e^{-i\varphi(z)-W(z)}. \tag{23}$$

Since the measurements of the reflection curve yielded the modulus of $R(y)$, while the values of $\varphi(0)$ and $W(0)$ in the regions $|v| > 1$ can be regarded as known, it follows that according to (18) the data on the angular dependence of the photoemission can be used to reconstruct also the phase of $R(y)$, i.e., to determine completely the reflection amplitude. On the other hand, according to (23) the quantity $R(v)$ in the region $|y| > 1$ is essentially the Fourier component of the function $f(z) = \exp[-i\varphi(z) - W(z)]$. A possibility is thus provided for reconstructing this function with the aid of an inverse Fourier transformation.

Consequently, simultaneous measurements of the reflection curves and of the photoemission in situations when the conditions (19) are satisfied make it possible in principle to reconstruct fully the perturbations of the crystal structure in the surface layer, including both the average displacements of the atomic planes $u(z)$, and the random displacements described by the static Debye-Waller factor $e^{-W(z)}$. The accuracy with which these parameters is determined depends, naturally, on the degree to which the inequalities (19) hold, on the accuracy of the experimental data, on the region of the angles y in which the measurements are made, and also on the angle width of the incident x-ray beam. Each of these questions calls for a special study.

Formula (18) was obtained in fact in the limit of an infinitesimally small depth L of photoelectron emergence. We obtain below a more general expression for $\varkappa(y)$ with allowance for the variation of the fields E_0 and E_h at the depth L. We find first the change of the wave field near the surface. The amplitudes of the field on the surface itself are assumed given:

$$E_0(0, y) = 1, \quad E_h(0, y) = \gamma\bar{\beta}R(y). \tag{24}$$

To find the fields $E_{0,h}(z)$ at $z > 0$ we use Eqs. (2), which are best recast in a somewhat different form by introducing the quantities $\bar{E}_{0,h}(z, y)$ defined by the relations

$$E_0(z) = \exp\left\{2i\frac{\chi_0}{\beta^{1/2}|\chi_{rh}|}z\right\}\bar{E}_0(z),$$
$$E_h(z) = \exp\left\{-2i\frac{\chi_0-\alpha}{\beta^{1/2}|\chi_{rh}|}z\right\}\bar{E}_h(z). \tag{25}$$

Here, as before, the unit of length is taken to be L_{ex} (14). For the amplitudes $\bar{E}_{0,h}(z)$ Eqs. (2) take the form

$$\frac{d\bar{E}_0}{dz} = i\frac{\chi_{\bar{h}}}{\beta^{1/2}|\chi_{rh}|}\exp[i\Phi(z,y)]\bar{E}_h,$$
$$\frac{d\bar{E}_h}{dz} = -i\frac{\beta^{1/2}\chi_h}{|\chi_{rh}|}\exp[-i\Phi^*(z,y)]\bar{E}_0, \tag{26}$$

where

$$\Phi(z,y) = \varphi(z) + iW(z) + 2yz. \tag{27}$$

Formula (5) for (y) is expressed in terms of $\bar{E}_{0,h}$ as follows:

$$\varkappa(y) = \frac{1}{l}\int_0^\infty dz P(z)\{|\bar{E}_0(z,y)|^2 + |\bar{E}_h(z,y)|^2$$
$$+ 2\,\text{Re}[e_{\bar{h}}\bar{E}_0^*(z,y)\bar{E}_h(z,y)\exp[i\Phi(z,y)]]\}, \tag{28}$$

where

$$l = \int_0^\infty dz P(z) = L/L_{ex}.$$

The amplitudes $\bar{E}_{0,h}$ are convenient in that, as can be seen from (26), they vary little over distances smaller than L_{ex}, whereas the amplitude $E_h(z)$ can vary strongly also over small distances, because of the presence of the additional phase factor. We seek a solution of the system (26) in the form

$$E_{0,h}(z) = E_{0,h}(0) + \Delta E_{0,h}(z). \tag{29}$$

In the approximation linear in the parameter l we have

$$\Delta E_0(z, y) = \frac{i\gamma\chi_{\bar{h}}}{|\chi_{rh}|}R(y)\int_0^z dz'\exp[i\Phi(z',y)], \tag{30}$$

$$\Delta E_h(z, y) = -i\frac{\chi_h}{|\chi_{rh}|}\beta^{1/2}\int_0^z dz'\exp[-i\Phi^*(z',y)].$$

Formula (28) with allowance for the obtained changes in the fields $\bar{E}_{0,h}(z)$ and with retention of only the terms linear in the parameter l can be easily reduced to the form

$$\varkappa(y) = (1+\beta^{1/2}f_1(y)) + \beta|R(y)|^2(1+\beta^{-1/2}f_1(y))$$
$$+ 2\beta^{1/2}\,\text{Re}[R(y)(e_{\bar{h}}\langle e^{i\Phi(z,y)}\rangle + f_2(y))]. \tag{31}$$

Here $f_1(y)$ and $f_2(y)$ are terms small in the parameter l:

$$f_1(y) = \left\langle 2\,\text{Im}\left(e_{\bar{h}}\frac{\chi_h}{|\chi_{rh}|}\int_0^z dz'\exp\{i\Phi(z,y)-i\Phi^*(z',y)\}\right)\right\rangle, \tag{32}$$

$$f_2(y) = i\frac{\chi_{\bar{h}}}{|\chi_{rh}|}\left(\beta^{1/2}+\frac{1}{\beta^{1/2}}\right)\left\langle\int_0^z dz'\exp\{i\Phi(z',y)\}\right\rangle.$$

We have introduced above the notation

$$\langle\ldots\rangle = \frac{1}{l}\int_0^\infty dz\ldots P(z). \tag{33}$$

We disregard first the correction terms connected with the functions $f_1(y)$ and $f_2(y)$. Then the fact that the

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photoelectrons emerge from a finite depth is reflected in formula (31) by the factor

$$\langle e^{i\Phi(z,y)} \rangle = \frac{1}{l} \int_0^\infty dz\, P(z)\exp\{i\varphi(z)-W(z)+2iyz\}, \qquad (34)$$

which goes over in the limit as $l \to 0$ into $\exp[i\varphi(0) - W(0)]$.

Naturally, allowance for the finite emergence depth leads primarily to a partial averaging-out of the phase factor $e^{i\varphi(z)}$. However, even if we assume that the change of the phase $\varphi(z)$ near the surface can be neglected, we still obtain a substantial deviation from formula (18), since the exponential of the integrand in (34) contains the term $2iyz$. The role of this term is negligible at values $|y| \ll \frac{1}{2}l$, but at $|y| \gtrsim \frac{1}{2}l$ there is already a noticeable averaging out of the factor (34). If the photoelectron emission probability is known, then this factor can be calculated directly.

The restriction on the weak change of the phase $\varphi(z)$ over distances on the order of l is quite strong and greatly decreases the region of applicability of (18) in real situation. The class of investigated perturbations can actually be greatly expanded. Assume that over distances on the order l it is not the phase which changes, but only its first derivative, i.e., assume that

$$\frac{\partial^2\varphi}{\partial z^2} l^2 \ll 1. \qquad (35)$$

In this case we can expand the phase $\varphi(z)$ in powers of z near $z = 0$ and confine ourselves to the linear term of the expansion

$$\varphi(z) = \varphi(0) - 2y_0 z. \qquad (36)$$

We assume also that the factor $e^{-W(z)}$ changes little over distances on the order l. We then readily obtain from (34)

$$\langle e^{i\Phi(z,y)} \rangle = e^{i\varphi(0)-W(0)} F(y-y_0), \qquad (37)$$

where

$$F(y) = \langle e^{2iyz} \rangle. \qquad (38)$$

The quantity y_0 determines precisely the angular position corresponding to exact satisfaction of the Bragg condition for a crystal lattice with the parameters of the immediate surface layer.

In the approximation (36), the functions $f_1(y)$ and $f_2(y)$ can also be expressed in terms of the function (38), namely

$$f_1(y-y_0) = 2\,\mathrm{Re}\left(e_{\bar{h}}\frac{\chi_h}{|\chi_{rh}|}e^{-2W(0)}\frac{1-F(y-y_0)}{2(y-y_0)}\right),$$

$$f_2(y-y_0) = -\frac{\chi_h}{|\chi_{rh}|}\left(\beta^{1/2}+\frac{1}{\beta^{1/2}}\right)e^{i\varphi(0)-W(0)}\frac{1-F(y-y_0)}{2(y-y_0)}. \qquad (39)$$

Thus, the problem reduces to finding the function $F(y)$. According to the presently held opinions, for electrons with given energy E_a the probability of emergence to the surface is described by the law

$$P_a(z) = \begin{cases} 1-z/l_a, & z<l_a \\ 0, & z>l_a \end{cases}, \quad l_a=\frac{L_a}{L_{ex}}, \qquad (40)$$

where L_a is taken to mean the so-called practical electron range, determined in experiment by shooting through thin films. A simple empirical formula was proposed in [18] for L_a of simple substances at energies from 0.1 to 10 keV:

$$L_a=6\cdot 10^{-5}AE_a^\gamma/\rho Z, \quad \gamma=1.3-1.5. \qquad (41)$$

Here ρ is the density of the material (in g/cm³), Z is the atomic number. A is the mass number, and E_a is the energy in keV.

The photoeffect is accompanied by formation of electron groups that vary in energy and correspond to transitions from the K, L, M, etc. atomic shells. We denote by n_a the probability of formation of electrons of group a. Then the total probability of the emergence of an electron from the crystal is given by

$$P(z) = \sum_a n_a P_a(z). \qquad (42)$$

Using (28), (40), and (42), we easily obtain

$$F(y) = \frac{i}{2yl}\sum_a n_a\left(1+\frac{1-\exp(2iyl_a)}{2iyl_a}\right),$$

$$l = \frac{1}{2}\sum_a n_a l_a. \qquad (43)$$

Formulas (31), (37)–(39), and (43) can be used for a much wider class of distortions than formula (18). To determine the amplitude $R(y)$ from these expressions, however, it is necessary to know the parameter y_0. In a number of cases, for example for monotonic distortion profiles, it can be estimated directly from the reflection curves and, as seen from (43), a rather rough estimate of this parameter with an uncertainty $\Delta y_0 \sim 1/l$ is sufficient. The general situation calls for a special analysis, and appropriate recommendations for the best method of determining y_0 can be obtained, in our opinion, in the analysis of the actual experimental material.

We note in conclusion that experimeters are well equipped for a realization of the conditions (19). Indeed, by changing the order of the reflection it is possible to vary L_{ex} in a wide range, and by varying the x-ray wavelengths it is possible in fact to vary the depth from which the photoelectrons emerge.[14] Of great interest from this point of view are experiments with separation of different groups of electrons. In the case of an ideal crystal, the separation yields practically no new results[19] but in the study of perturbed layers this method can turn out to be very effective.

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Excitation and propagation of phonons in anthracene crystals

V. L. Broude, N. A. Vidmont, D. V. Kazakovtsev, V. V. Korshunov, I. B. Levinson, A. A. Maksimov, I. I. Tartakovskii, and V. P. Yashnikov

*Institute of Solid State Physics, USSR Academy of Sciences
and L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences*
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The time dependence of the luminescence of thin anthracene plates excited by pulsed lasers is investigated. It is shown that the half-widths of the bands in the investigated spectra can be used to estimate the number of nonequilibrium phonons produced in the sample as a result of relaxation of the electronic excitations. Qualitative models of generation and propagation of nonequilibrium phonons in a planar sample geometry are constructed. It is shown that the experimental observations are in satisfactory agreement with the model-deduced premises.

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1. INTRODUCTION

The luminescence of anthracene is accompanied, as is the case for other molecular crystals, by a heat release (creation of additional phonons), and the energy efficiency of the radiation, in contrast with the quantum efficiency, is not equal to unity. This is connected primarily with the preceding act of luminescence by the process of fast (≤ 0.1 nanosec) light-induced electron excitation to the lowest exciton band. Second, there takes place, at least partially, further relaxation of the exciton states, for example, with participation of those lying below the triplet-exciton bands. In anthracene crystals, of course, this process is less probable than the direct luminescence of excitons (the exciton lifetime is $\tau_e = 3$ nanosec) and the quantum efficiency of luminescence

at low pumping is close to unity. Finally, as a result of the luminescent electron transitions, the developed system of vibrational sublevels of the ground state is filled with nonequilibrium phonons.

Additional channels of heat release arise with increase in the intensity of the light that excites the luminescence. They are produced by the interaction of excitons and depend in nonlinear fashion on their concentration. Evidently, the Auger recombination of excitons is most effective for the heat release. In this recombination, one of the colliding excitons receives the energy of the other. The resulting high electron excitation again relaxes to the lowest exciton band. Under these conditions, a drop is experimentally observed in the energy yield of the radiation, to 0.1 and below, i.e., practically all the light energy incident on the crystal is transformed into phonons.

In the first stage of relaxation of the electron excitation, high-frequency optical phonons are generated (intramolecular vibrational modes). Further relaxation is accompanied by the breaking down of the intramolecular phonons and it is concluded at some stage with the formation of acoustical phonons that are distributed uniformly over the Brillouin zone. The entire process of relaxation, except the very last, can be regarded as spatially localized, since the exciton bands, and especially the bands of optical vibrations, are relatively narrow and the free paths of these excitations are small.