
DIFFRACTION AND SCATTERING OF IONIZING RADIATIONS

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Program for Calculating the Scattering Parameters Used in the X-ray Standing Wave Method

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Abstract—A computer program for calculating the complex kinematic scattering parameters χ_0 , χ_h , and $\chi_{\bar{h}}$ of X rays, which are Fourier components of the crystal complex susceptibility, as well as some of their combinations, is presented. The values calculated by the program can be used for computer simulation of experimental results obtained by the X-ray standing-wave method. Methods for calculating these parameters on the basis of well-known tables are described in detail. For crystals of complex structure, it is necessary to know their structure and the Debye temperature or specific heat capacity in order to calculate χ_h and $\chi_{\bar{h}}$. To calculate χ_0 , it is sufficient to know the chemical formula and the density of a material.

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INTRODUCTION

The X-ray standing-wave method implies measurement of the angular dependence of the yield of secondary radiations under the conditions of dynamic X-ray diffraction in perfect crystals or in crystals with a deformed crystal lattice (see, for example, [1–3]). Generally, electron photoemission (external photoelectric effect) and the fluorescence of atoms of any sort of the main crystal matrix or impurity atoms are measured. Most often, the symmetric double-crystal dispersionless scheme of diffraction in reflection (the Bragg geometry) is used, where a standing wave is formed along the normal to the surface. In this case, the experimental angular dependences of the X-ray reflection and the secondary radiation yield depend only on the lattice strain along the normal to the surface. This strain arises upon treatment of surface layers of semiconductor crystals by different methods, for example, diffusion or ion implantation of impurities and growth of epitaxial films on the surface of an ideal substrate.

Determination of the strain profile in a sample from the shape of the angular dependences of the X-ray reflection and secondary radiation is the main purpose of the X-ray standing-wave method. Generally, it is a very difficult problem since an experimental result depends on a large number of parameters. Until now, it has been solved only by theoretical simulation of the experiment and choice of such scattering parameters for which the theoretical and experimental curves almost coincide. It is convenient to model a crystal

deformed along the normal to surface by a multilayer crystalline system composed of several layers with an ideal crystal lattice but different scattering parameters in each layer. For a slowly varying strain, the number of layers can be large, but in the case of epitaxial structures one or two layers on the substrate may be sufficient. The calculation formulas and the description of the computer program for calculating such a model were reported in [4].

Nevertheless, there is a problem of correct determination of the main scattering parameters in such layers, which should be set relatively exactly. Only in this case will the determined variable parameters correspond to reality. Note that the moduli and the phase difference of the complete Fourier components of the crystal polarizability can be obtained on the Internet [5] by way of Stepanov's online program. However, these data are insufficient for application of the X-ray standing-wave method. In addition, such an approach does not allow one to correct the calculation program and cannot be used for the crystals that are not included in the database. This is especially urgent for epitaxial films of variable composition. Therefore, another, more flexible program is necessary in order to allow a user to construct a personal database for required crystals and obtain all parameters that are necessary for calculating the secondary radiation yield. In this paper, we describe such a program and report the calculation formulas that are used in it.

FOURIER COMPONENTS OF POLARIZABILITY

The polarizability $X(\omega)$ of a medium in the X-ray range can be determined from the relation between the complex amplitude $E(\omega)$ of the radiation electric field and the amplitude of the electric current induced by this field by the formula $j(\omega) = (\omega/4\pi i)X(\omega)E(\omega)$. The main process is the Rayleigh scattering, i.e., the elastic scattering of a photon from electrons. This process is classical; therefore, the correct value is obtained even with the use of the Newtonian mechanics. The electric field acts on an electron with the force eE , where e is the elementary charge. Accordingly, the field-induced acceleration of the electron can be found from the Newton equation, while the current is $e v$, where v is the induced electron velocity. As a result, we have

$$m \frac{dv}{dt} = eE(\omega) \exp(-i\omega t),$$

$$j(\omega) = e v(\omega) = \frac{ie^2}{m\omega} E(\omega). \quad (1)$$

From the second relation, taking into account the polarizability definition, we obtain

$$X(\omega) = -\frac{4\pi e^2}{m\omega^2} = -\frac{\lambda^2 r_0}{\pi}, \quad r_0 = \frac{e^2}{mc^2}, \quad \frac{2\pi}{\lambda} = \frac{\omega}{c}. \quad (2)$$

Here, r_0 is the classical radius of an electron, λ is the X-ray wavelength, and c is the speed of light.

Formula (2) describes the contribution of a single electron to the polarizability. The polarizability of a crystal is determined for its volume unit. Accordingly, the zeroth Fourier component of polarizability will be obtained through multiplication of formula (2) by the number of electrons per volume unit. With allowance for the crystal structure, this number can be divided into two components, specifically, the number of unit cells in a crystal, which is equal to V_0^{-1} (V_0 is the unit-cell volume), and the number of electrons per unit cell. It is convenient to represent the latter component as a sum of the products of the number of electrons in each atom and the number of such atoms per unit cell.

In addition, the corrections to other scattering processes should be taken into account. The main process of such processes is the photoelectron absorption. This is a quantum process and its calculation is a fairly difficult problem. Photoelectron absorption corresponds to transitions between discrete electronic states in an atom; therefore, it resonantly depends on frequency and is described by the imaginary part of polarizability. The corrections related to the photoelectric effect are generally referred to as the dispersion corrections. Sometimes, an additional correction related to the inelastic Compton scattering may contribute to the imaginary part of polarizability, i.e., to the absorption, especially at high photon energies (exceeding 30 keV). Let us

write the formula for the zeroth Fourier component of polarizability in the form

$$\chi_0 = -\frac{\lambda^2 r_0}{\pi V_0} \sum_j N_j [Z_j + \Delta f_1(j) - i(f_2(j) + \Delta f_2(j))]. \quad (3)$$

Here, the sum is over the types of atoms: N is the number of atoms of a given type, Z is the number of electrons per atom (the atomic number), $\Delta f_1 = (f_1 - Z)$ is the correction to the number of electrons due to the photoelectric effect, f_2 is the contribution of an atom to the imaginary part due to the photoelectric effect, and Δf_2 is the correction to f_2 due to the Compton scattering.

This form is convenient because the sum in square brackets describes processes at the single-atom level. In Henke's tables and other similar tables (see, for example, [6]), the number of electrons Z in the scattering amplitude at the atomic level is replaced with the complex quantity $f_1 - if_2$. The imaginary part of this quantity is generally derived from the experimental values of the absorption coefficients and Δf_1 is derived from the imaginary part with the use of the dispersion relations. The latter link the real and imaginary parts of polarizability and are a consequence of the causality principle. The additional correction Δf_2 that is due to the Compton scattering is not taken into account in the above-mentioned tables and should be calculated separately. Note that the photon absorption in the photoelectric effect has been theoretically calculated also (see, for example, [7]).

The Fourier component of polarizability on the reciprocal lattice vector \mathbf{h} should take into account the actual spatial distribution of electrons in a crystal. In the case of the Rayleigh scattering, this characteristic depends, in particular, on the spatial distribution of electron density in an atom. Obviously, the valence-electron density of an atom in a crystal may differ from that in a free atom. However, this deviation is apparently small and, until now, no attempts have been made to calculate it. Concerning the Fourier component of the electron density of free atoms, such calculations have been performed repeatedly in different approximations. The most reliable results were obtained in the Hartree-Fock relativistic approximation and reported in the form of tables in [8]. Since an atom is spherically symmetric, the calculated function $F_A(s)$ depends only on the modulus of the reciprocal lattice vector and is generally written as a function of the argument $s = |\mathbf{h}|/4\pi = \sin \theta_B/\lambda$, where θ_B is the Bragg angle. For crystals with a rectangular lattice, $|\mathbf{h}| = 2\pi[(h/a)^2 + (k/b)^2 + (l/c)^2]^{1/2}$, where h , k , and l are the Miller indices of the corresponding reflection and a , b , and c are the lattice constants.

An additional source of the spatial change in the electron density is the thermal vibrations of atoms.

Their effect on the Fourier component of electron density is taken into account by the thermal factor

$$F_T(s) = \exp(-|\mathbf{h}|^2 \langle u^2 \rangle / 2), \quad (4)$$

where $\langle u^2 \rangle$ is the mean-square atomic displacement from a lattice site. The square of $F_T(s)$ is equal to the Debye–Waller factor. In addition, it is necessary to take into account the phase factors arising for the atoms that are not located at the center of a unit cell. These phase factors are determined by the position of atoms and are independent of their sort. Therefore, a new factor will appear in the sum over the types of atoms, which is referred to as the structure factor. In this factor, it is necessary to perform summation over all possible coordinates of the atoms of a specific type:

$$S(\mathbf{h}) = (1/k_m) \sum_k \exp(i\mathbf{h}\mathbf{r}_k), \quad (5)$$

where k_m is the maximum number of positions that can be occupied by an atom of a specific type. Note that atoms of each type generally have their own coordinates and, in this case, $k_m = N$. However, in some epitaxial structures, atoms of different types substitute for each other at the same positions. In this case, $k_m > N$.

Concerning the dispersion and absorption corrections, their dependence on the reciprocal lattice vector is weak and can be neglected in calculations of the Fourier components of polarizability by the X-ray standing-wave method. As a result, we obtain the formula

$$\chi_h = -\frac{\lambda^2 r_0}{\pi V_0} \sum_j N_j [F_A(s, j) + \Delta f_1(j) - i(f_2(j) + \Delta f_2(j))] F_T(s, j) S(\mathbf{h}, j). \quad (6)$$

An analogous parameter for the reciprocal lattice vector with a minus sign, $\chi_{\bar{h}}$, is obtained from formula (6) via replacement of $S(\mathbf{h}, j)$ with a complex conjugate value. In crystals with an inversion center, $\chi_h = \chi_{\bar{h}}$ and the structure factor $S(\mathbf{h})$ does not have an imaginary part; therefore, the imaginary parts of all parameters are related only to the absorption.

Formula (6) corresponds to the σ polarization of an X-ray wave. In this case, the electric field vector is directed perpendicularly to the scattering plane. This polarization is conventional when synchrotron radiation is used. In the case of unpolarized radiation, it is additionally necessary to take into account the π polarization, in which expression (6) is multiplied by the polarization factor. For the dipole interaction (Rayleigh scattering and the main part of photoelectron absorption), this factor is equal to $\cos(2\theta_B)$. For the quadrupole correction to the photoelectron absorption and for the Compton scattering, the dependence on polarization is different. However, these contributions are small and become significant only in the investigation of the

multiwave effect of anomalous transmission (see, for example, [9]). In calculations by the X-ray standing-wave method, it is sufficient to take into account the polarization (when necessary) at the level of dipole interaction. This approach is used, for example, in the program proposed in [4].

Calculation of χ_0 . The zero Fourier component of polarizability describes the coherent forward scattering for radiation in the form of a plane wave. It is important not only in diffraction experiments but also in numerous absorption or phase contrast investigations. In these experiments, a beam that passes through a sample does not change its direction, and the specific sample structure can even be unknown in this case. The value of χ_0 can be calculated from the known chemical formula of the sample material and its density. The chemical formula gives information about the types of atoms and the numbers of atoms of each type, while the number of molecules per volume unit is obtained by dividing the density ρ of the material (in g/cm^3) by the molecule mass (in grams). It is convenient to divide the density by the mass of a molecule M_m (in au) and multiply the result by Avogadro's number. As a result, formula (3) can be rewritten in the form

$$\chi_0 = -8.303 \times 10^{-4} \frac{\rho}{M_m E^2} \quad (7)$$

$$\times \sum_j N_j [f_1(j) - i(f_2(j) + \Delta f_2(j))].$$

Here, N_j is the number of atoms of the j th type in a molecule and E is the photon energy (in keV).

The parameters f_1 and f_2 are calculated by interpolation of the corresponding tables, which can be obtained on the Internet, either with the distributive of the XOP program [10] or directly [11]. The program uses the values from the flf2_Windt.dat file in the range from 1 to 100 keV. The correction due to the Compton scattering is calculated through the interpolation formula [12]

$$\Delta f_2(E, j) = 1.4312 \times 10^{-5} E \exp\left(\sum_{k=0}^3 C_{kj} [\ln(E)]^k\right). \quad (8)$$

The values of the coefficients C_0 , C_1 , C_2 , and C_3 for 94 chemical elements were taken from [12].

Calculation of χ_h . To calculate the diffraction parameter, it is necessary to know the crystal structure because it determines the structure factors $S(\mathbf{h}, j)$. In experiments, the standing-wave method can be used to investigate samples with a very complex structure; therefore, it is unrealistic to develop a database of all structures. Calculation of the structure factors should be performed independently—only in this case can a program be universal. Concerning the atomic scattering factor $F_A(s)$, it is convenient to calculate it from again

the interpolation formula, which in this case has the form

$$F_A(s) = \sum_{k=1}^4 a_k \exp(-b_k s^2) + c. \quad (9)$$

The coefficients a_k , b_k , and c are known for all practically important elements [13].

Let us consider the procedure of calculation of the thermal factor $F_T(s)$. In a strict sense, this factor depends on the type of an atom. However, such dependences have not been theoretically calculated, since such a calculation requires knowledge of the density of phonon states for each specific atom in a specific compound. Finding of such data is a very difficult problem. In some experimental studies, the values of mean-square atomic displacements $\langle u^2 \rangle$ were reported for each type of atoms in crystals with a complex chemical composition (see, for example, [14]). These values can be used for direct calculation of the thermal factor by formula (4). However, there are very few such data.

Concerning relatively simple crystals, it is known that the thermal factor is determined mainly by the long-wavelength lattice vibrations (acoustic phonons), in which a unit cell moves as a whole. For this reason, the dependence on the type of an atom can be neglected, and a unified factor can be considered for all atoms. Using an average value $\langle u^2 \rangle$ (see, for example, [15]), one can calculate the average thermal factor by formula (4).

The other way consists in parameterizing the density of states of acoustic phonons by a single parameter—the Debye temperature T_D . The Debye model is used, which gives the formula

$$F_T(s) = \exp(-B(T)s^2),$$

$$B(T) = \frac{6h^2}{M_a k_B T_D} \left(\frac{1}{4} + \frac{1}{x^2} \int_0^x dz \frac{z}{(\exp(z) - 1)} \right), \quad (10)$$

$$x = \frac{T_D}{T},$$

where h is Planck's constant, M_a is the average mass of an atom, and k_B is the Boltzmann constant. If s has a dimension of 10^8 cm^{-1} , the mass of an atom is measured in au, and the Debye temperature is measured in K, the coefficient in the formula for $B(T)$ before the parentheses is $11\,490.4/(M_a T_D)$.

In general, the Debye temperature should be determined from the results of special X-ray diffraction experiments. However, only a few such experiments have been performed. The corresponding studies were reviewed in [16]. If such data are absent, one can use the value of T_D that is obtained from the measurements of specific heat at low temperatures. For monoatomic crystals, such values of T_D are known for almost all ele-

ments (see, for example, [17]). As is known, the formula for the specific heat C_V in the Debye model has the form [17]

$$C_V = 9 \frac{k_B}{M_a x^3} \int_0^x dz \frac{z^4 \exp(z)}{(\exp(z) - 1)^2}, \quad x = \frac{T_D}{T}. \quad (11)$$

If the average mass of an atom is measured in au and C_V is measured in $(\text{J}/(\text{g K}))$, the coefficient before the integral is $74.82/(M_a x^3)$. At low temperatures, i.e., at large x , the integral tends toward a constant equal to $4\pi^4/15 = 25.98$.

When the Debye temperature is unknown, it can be determined from the known specific heat by formula (11). Unfortunately, the value of C_V in tables is generally given at room temperature when formula (11) is insufficiently correct, especially for materials with a low Debye temperature. If C_V is calculated by formula (11) at room temperature with the use of known values of average atomic mass and the Debye temperature, the values obtained are always smaller than the experimental ones, although the difference is insignificant. However, the inverse problem of calculation of the Debye temperature from a known value of C_V is extremely sensitive to overestimated values and sometimes cannot be solved at all. The reason is that, according to formula (11), C_V has a finite maximum value at $T_D = 0$, which is equal to $3k_B/M_a$. Concerning the compounds with a variable composition, there are generally no data for them. In this case, one can use the values obtained by interpolation among the compounds for which T_D is known.

In the standing-wave method as applied to measurement of fluorescence, according to [4], it is additionally necessary to know the partial values $\chi_{i\bar{h}}(j)/\chi_{i0}(j)$, i.e., the ratio of the Fourier components of the imaginary part of polarizability for a certain type of atoms that make a contribution to the fluorescence signal recorded. The modulus of this expression in the approximation under consideration is equal to the product of the thermal factor and the modulus of the structure factor, and the phase is equal to the phase of the structure factor. In the program, along with the values of χ_h , the parameters $X = (\chi_h \chi_{\bar{h}})^{1/2}$ and $Y = (\chi_h / \chi_{\bar{h}})^{1/2}$ are calculated also. The listing contains the parameters $f_1, f_2, \Delta f_2$, and F_A for each type of atoms and the thermal factor F_T when it is calculated by formula (10). The specific organization of the input and output data of the program is not described here, since it may change in the long run. This information can be obtained directly from the technical documentation for the program.

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