

# Calculation of the polarizabilities of crystals for diffraction of x-rays of the continuous spectrum at wavelengths of 0.1–10 Å

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(Submitted June 15, 1990)

*Kristallografiya* 36, 856–860 (July–August 1991)

The authors describe algorithms and a program for calculating the polarizabilities of single crystals for dynamic diffraction of synchrotron and x-radiation with a continuous spectrum in the wavelength range 0.1–10 Å. The calculation is made on the basis of data of various x-ray spectral tables without calculation of the wave functions of the atoms. The authors suggest new methods of interpolation of the absorption coefficients and dispersion corrections.

Existing tables of parameters for diffraction of x rays in the middle range of wavelengths by crystals are primarily oriented to the characteristic lines, and therefore until recently in most experiments use has been made of the intense lines of the characteristic spectrum of x-ray tubes (see, e.g., Refs. 1 and 2).

However, in recent years in x-ray diffractometry, sources with a continuous spectrum have been developed and increasingly widely used. We refer primarily to synchrotron radiation, the spectral brightness of which is several orders of magnitude greater than that of ordinary x-ray tubes, opening

in principle new possibilities in x-ray optics and x-ray diffraction analysis of crystals. On the other hand, we must mention such a promising source as Čerenkov x radiation,<sup>3</sup> the brightness of which, in a pulse lasting several nanoseconds, may reach about  $10^9$  quanta with a high degree of collimation of the x-ray beam.

For effective use of the new x-ray sources we must know the parameters of scattering by crystals for radiation with an arbitrary wavelength. In this article we attempt to solve this problem by relatively simple means on the basis of interpolation of the data from existing tables. We describe

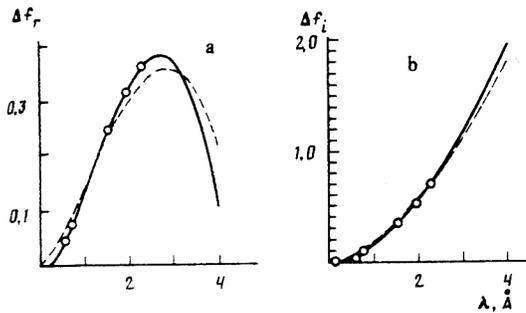


FIG. 1. Dependences of dispersion corrections, real  $\Delta f_r$  (a) and imaginary  $\Delta f_i$  (b), on wavelength  $\lambda$ . Dashed curves: dependences calculated from Eqs. (6), (7) with oscillator forces from tables. Solid curves: results of interpolation of tabulated values<sup>10</sup>; circles: tabulated values of dispersion corrections.

algorithms and a program in Fortran, realized on many types of computers.

### SURVEY OF THEORY AND FORMULATION OF PROBLEM

Expressions for the complex polarizabilities of ideal absorbing crystals in the x-ray wavelength range are given in many sources (see, e.g., Ref. 4):

$$\chi_{0r} = -(\lambda^2 r_0 / \pi \Omega) \sum_{j=1}^N (f_j(0) + \Delta f_{rj}), \quad (1)$$

$$\chi_{hr} = -(\lambda^2 r_0 / \pi \Omega) \sum_{j=1}^N e^{-W_j(s)} (f_j(s) + \Delta f_{rj}) e^{ihr_j}, \quad (2)$$

$$\chi_{0i} = -(\lambda / 2\pi \Omega) \sum_{j=1}^N (\sigma_j^p + \sigma_j^q), \quad (3)$$

$$\chi_{hi} = -(\lambda / 2\pi \Omega) \sum_{j=1}^N e^{-W_j(s)} \sigma_j^p e^{ihr_j}. \quad (4)$$

Here the subscript  $r$  denotes the real part of the Fourier component of the polarizability,  $i$  the imaginary part; the sum is taken over  $N$  atoms in the unit cell of the crystal with coordinates  $r_j$ ;  $\lambda$  is the wavelength of the x rays,  $r_0$  is the classical radius of the electron,  $\Omega$  is the volume of the unit cell,  $\Omega = abc$  where  $a$ ,  $b$ ,  $c$  are the unit-cell parameters in the orthogonal setting,  $\mathbf{h}$  is the reciprocal-lattice vector for the family of planes with indices  $(hkl)$  at which diffraction occurs, and  $s = 1/(2d)$ , where  $d = ((h/a)^2 + (k/b)^2 + (l/c)^2)^{-1/2}$  is the interplanar distance.

Under the summation sign there are the following scattering parameters of the atoms in the unit cell of the crystal.

1.  $f(s)$  is the amplitude of scattering of x rays by an atom, normalized in such a way that  $f(0)$  is equal to the number of electrons in the atom. For  $f(s)$  there is the interpolation expression

$$f(s) = \sum_{i=1}^4 a_i e^{-b_i s^2 + c}, \quad (5)$$

where the parameters  $a_i$ ,  $b_i$ , and  $c$  are tabulated for practically all the elements in Refs. 1, 5, and 6.

2.  $\Delta f_r$  is the real part of the dispersion correction. The dispersion correction depends on the wavelength of the radiation and the type of atom, but is practically independent of the angle of scattering (indices of reflection). There are two methods of calculating the dispersion corrections.

The first method was suggested in Refs. 7 and 8. In this method the corrections are calculated by means of the expressions

$$\Delta f_r = \sum_{k=1}^{N_s} g_k P(X_k, N_k), \quad (6)$$

$$\Delta f_i = 0.5\pi \sum_{k=1}^{N_s} g_k (N_k - 1) / X_k^{N_k - 1}. \quad (7)$$

Here  $\Delta f_i$  is the imaginary part of the dispersion correction. The summation in (6)-(7) is taken over the absorption edges,  $N_s$  is the number of absorption edges taken into account,  $N_k = 11/4$  for the  $s$  electrons of the first shell of the atom,  $N_k = 7/3$  for the  $s$  electrons of the second shell,  $N_k = 5/2$  for all the remaining electrons,  $P(X_k, N_k)$  is the integral evaluated in Ref. 9,  $X_k = \lambda/\lambda_k$  is the ratio of the wavelength of the radiation to the wavelengths of the absorption edges, and  $g_k$  are the forces of the oscillators at the absorption edges.

To use this method we must know  $\lambda_k$  and  $g_k$ . The parameters  $\lambda_k$  are given, for example, in Ref. 2; the forces of the oscillators are given in Ref. 7, regrettably only for a small number of elements.

The second, more exact method of calculating the dispersion corrections on the basis of the quantum-mechanical relativistic wave functions of the atoms, calculated in the Dirac-Slater approximation, is given in Refs. 8 and 10. On the basis of this method in Refs. 7, 8, 10 there were published the dispersion correction for most elements for five characteristic wavelengths  $\text{CrK}\alpha_1$ ,  $\text{FeK}\alpha_1$ ,  $\text{CuK}\alpha_1$ ,  $\text{MoK}\alpha_1$ ,  $\text{AgK}\alpha_1$ . However, calculation by this method for arbitrary wavelengths is impossible without a knowledge of the wave functions.

In this connection the question of interpolation of the dispersion corrections will be analyzed by us in the next section.

3.  $e^{-W(s)}$  is the Debye-Waller temperature factor. The dependence  $W(s)$  is expressed in the form

$$W(s) = Bs^2, \quad (8)$$

where  $B = B(x)$  is the Debye coefficient:

$$B(x) = (12h^2/mkT_D) (\Phi(x)/x + 1/4), \quad (9)$$

$x = T/T_D$  is the ratio of the temperature of the crystal to the Debye temperature of the atom,  $h$  and  $k$  are Planck's and Boltzmann's constants,  $m$  is the mass of the atom, and  $\Phi(x)$  is the error integral, determined, for example, in Ref. 4.

Thus the temperature factor of the atom can be calculated in the presence of data either for  $T_D$  or for  $B$ . Tables of  $B$  (at room temperature) for a number of elements are given in Ref. 2, 7, and 11. Unfortunately, these parameters are not

known for all the elements, and moreover they depend not only on the species of atom but also on the type of crystal in which this atom occurs. However, for the medium and light atoms in view of the small influence of the temperature factor we can use the mean values of  $T_D$  and  $B$  over various structures.

4.  $\sigma^D$  and  $\sigma^Q$  are the dipole (with allowance for the dipole-octupole contribution) and quadrupole contributions to the photoelectric section of absorption of x rays by the atom. The quadrupole contribution is a small number, taken into account only in analysis of the Borrmann effect.

The most convenient method of calculating the cross sections of absorption on the basis of the hydrogen-like model of the atom for elements with numbers  $Z = 6-54$  is given in Ref. 12. The expressions are given for arbitrary values of  $\lambda$ . For calculations it is necessary to know the wavelengths of the absorption edges of the element, given in Ref. 2, and the shell screening constants, given in Ref. 4.

For  $Z < 6$  and  $Z > 54$  the method in Ref. 12 gives large errors. In this case we can calculate the absorption cross sections in terms of the mass coefficients of absorption  $\mu/\rho$  or in terms of the imaginary parts of the dispersion correction  $\Delta f_i$ .

In the first variant we use the relation

$$\sigma^D = (\mu/\rho)(A/N_A), \quad \sigma^Q = 0, \quad (10)$$

where  $A$  is the atomic weight of the element in amu, and  $N_A$  is Avogadro's number. The coefficients  $\mu/\rho$  are given in many tables (e.g., in Refs. 1, 2, 8) for the characteristic wavelengths. For the continuous spectrum we can use the interpolation expression from Ref. 1,

$$\mu/\rho = C\lambda^3 - D\lambda^4, \quad (11)$$

where  $C, D$  are given in Ref. 1 for several elements. Note that method (11) has poor accuracy, since it does not take account of discontinuities in the absorption.

The relation of the absorption cross section to the imaginary part of the dispersion correction takes the form

$$\sigma^D = 2\lambda r_0 \Delta f_i, \quad \sigma^Q = 0. \quad (12)$$

This method takes account of discontinuities in the absorption; however, as shown above, in the calculation of the dispersion correction there are also certain difficulties.

Thus to calculate the polarizabilities of crystals in the continuous spectrum it is necessary to solve the problem of interpolation of the absorption cross section for the elements with  $Z < 6$  and  $Z > 54$  and of the dispersion correction based on the accessible parameters — the values of  $\mu/\rho$ ,  $\Delta f_r$ ,  $\Delta f_i$  for the characteristic wavelengths. The remaining calculations present no difficulty on the basis of the following initial parameters: the wavelength of the x rays  $\lambda$ ; the characteristics of the crystal: symmetry, lattice constants  $a, b$ , and  $c$ , the indices of the reflection  $hkl$ , and the chemical composition and the coordinates of the atoms  $r_j$  in the unit cell; and the parameters of the elements constituting the crystal: the coefficients of the interpolation formula  $a_i, b_i, c$ , the Debye coefficients  $B$  or the values of the Debye temperature  $T_D$ , and the wavelengths of the absorption edges  $\lambda_k$ .

## INTERPOLATION OF DISPERSION CORRECTION AND ABSORPTION CROSS SECTIONS

To calculate the dispersion corrections with unknown oscillator forces at the edges, we proposed a method of interpolation of the tabulated values of the dispersion corrections for fixed wavelengths from Refs. 7, 8, and 10, or from other tables, e.g., Ref. 13.

We suppose that Eqs. (6), (7) hold for a limited interval of wavelengths; the oscillator strengths in these equations are the desired interpolation coefficients. In accordance with the number of absorption edges (i.e., interpolation coefficients), from the tables in Ref. 8 we take a certain number of dispersion correction  $\Delta f_r$  and  $\Delta f_i$  for the characteristic wavelengths. We choose corrections for the lines closest to a given wavelength. On the basis of expressions (6), (7) we compile a system of linear equations for the oscillator forces at the edges. The number of equations in the system is equal to the number of absorption edges; therefore the number of absorption edges should not exceed the number of known dispersion correction (10 for the tables in Ref. 7). The system is solved by Gauss's method.

On the basis of the obtained interpolation coefficients from Eqs. (6), (7) we calculate  $\Delta f_r$  and  $\Delta f_i$  for the given wavelength. In Fig. 1a, b we show the dependences  $\Delta f_r(\lambda)$  and  $\Delta f_i(\lambda)$  calculated by the above method for an Si atom from the values in the tables in Ref. 10. The circles mark the tabulated values from Ref. 10. The dashed curves show the dependences  $\Delta f_r(\lambda)$  and  $\Delta f_i(\lambda)$  calculated from Eqs. (6), (7) with substitution of the oscillator forces from Ref. 7. Clearly, the interpolation correctly reflects the variation of the dispersion corrections; the method cannot be used near the absorption edges.

In calculation of the dipole absorption section, on the basis of the method (11), refinement of  $C$  and  $D$  with respect to  $\mu/\rho$  from the tables in Ref. 1 is effected by their interpolation. We choose the values of  $\mu/\rho$  for two characteristic wavelengths closest to the given wavelength. Thus we obtain a system of two linear equations in  $C$  and  $D$ , which are solved by Kramer's method. We substitute for  $C$  and  $D$  in Eq. 11, and for the given value of  $\lambda$  we find  $\mu/\rho$ , and then  $\sigma^D$ .

## STRUCTURE OF PROGRAM

On the basis of the above methods we have developed a program for calculating the polarizabilities of crystals for the continuous x-ray spectrum. The program is intended for use in the conversational mode; all the experimental parameters (wavelength of radiation, denomination of crystal structure, chemical composition, lattice parameters, and indices of diffraction reflection) can be input from the keyboard.

In operating the program we use four files of the data base.

The file COORD.DAT contains data on the crystallographic structures. From the given structural code the program finds the type of symmetry, the number of components of the crystal, and their coordinates in the unit cell. The COORD.DAT file is organized in such a way that we can describe not only the class of structure (e.g., a structure of the diamond type), but also the particular structures, i.e.,

including data on the chemical composition and the values of the lattice parameters. In this case the number of parameters inquired for is reduced to a minimum – the wavelength, the structural code, and the indices of the reflection.

In the file ATOM.DAT we find information on the separate chemical elements. First, for each element we indicate the means of calculation of the structural amplitude, the dispersion corrections, the absorption cross section and the Debye–Waller factor. Also given are the parameters required for realization of any particular method of calculation.

In the other two files of the database we write the characteristic wavelengths of the x rays (for calculations of the discrete spectrum) and the reference parameters of the lattice for some crystals.

The database files are compiled with the aid of text editors and can be continually expanded to include new information.

The program envisages calculation of the polarizabilities both for pure crystals and for solutions of substitution (of the CdPbTe type) on account of a factor of filling of their sites by the atoms.

In conclusion we note that there is a version drawn up in the form of a subroutine. The program is oriented to IBM PC

compatibles; however, it can be ported to other platforms and at present also functions on SM and ES computers.

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Translated by S. G. Kirsch