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A new method for calculation of crystal susceptibilities for X-ray diffraction at arbitrary wavelength

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A novel method for the calculation of the X-ray susceptibility of a crystal in a wide range of radiation wavelengths is described. An analytical interpolation of one-electron wave functions is built to approximate the solution to Hartree–Fock equations for all atoms and ions of the periodic system of elements with high accuracy. These functions allow the calculation of the atomic form factors in the entire range of a transmitted momentum as well as the description of their anisotropy taking into account external and intracrystalline fields. Also, an analytical approximation for the force matrix of an arbitrary crystal is obtained and the microscopic calculation of the Debye–Waller factor for crystals with a complicated unit cell is presented.

1. Introduction

The complex X-ray susceptibility (XS) is a basic characteristic of a perfect crystal. The accuracy of XS calculations defines the reliability of spectra interpretation in diffraction experiments. The calculation of XS at an arbitrary wavelength also becomes very important in view of recent wide usage of synchrotron radiation (Authier, 1996) and development of new X-ray sources with a smoothly tuning frequency (Feranchuk *et al.*, 2000). The general definition of XS is well known (Pinsker, 1978), and there are several efficient programs to calculate it (Brennan & Cowan, 1991; Lugovskaya & Stepanov, 1991), available as commercial and shareware diffraction software. However, accuracy and diversity of modern experiments make it necessary to improve the algorithms for XS calculation. The accuracy of calculated XS values depends on the calculation method of its components (Pinsker, 1978) including (i) the atomic scattering factor (ASF) $f_0(s)$ in a wide range of the transmitted wave-vector s changes; (ii) Debye–Waller factor (DWF) $\exp[-W(s)]$; (iii) corrections for anormal dispersion $f' + if''$ and the structural phase factor defined by the atom's coordinates in the unit cell. The values of f' and f'' are tabulated in several reliable databases (for example, Sasaki, 1989, 1990), the nucleus coordinates for structure factors are also reportedly known from identification of the crystal structure. Therefore, in the present work emphasis is placed on the calculation of the ASF and DWF.

The value $f_0(s)$ is *ab initio* defined in *International Tables for Crystallography* (1992) by a Fourier image of the electron density of the atom (ion), found on the basis of Hartree–Fock (HF) wave functions. Unfortunately, this straightforward approach is not effective in practical calculations because of the necessity to use bulky databases for numerical solutions of the HF equations (Clementi & Roetti, 1974). The model of Tomas–Fermi (*International Tables for Crystallography*, 1992), also used for calculation of atomic form factors, is convenient for preliminary evaluation of XS but is not sufficient for analysis of precise experiments. The most effective model for this purpose is proved to be an analytical parametrization of the functions $f_0(s)$ presented by Cromer & Mann (1968) for most of the atoms and ions, and these data are used in the software packages (Brennan & Cowan, 1991; Lugovskaya & Stepanov, 1991). The tables of phenomenological parameters (Cromer & Mann, 1968) have been received for ASF as a result of numerical interpolation of the HF form factors in the interval of values $0 < s < 2$. This interpolation does not concern the functions themselves. Waasmaier & Kirfel (1995) have extended the $f_0(s)$ database to a larger interval of s using an extended set of parameters. However, both approaches do not allow corrections to be calculated to the ASF caused by the non-sphericity of the electron density of the atom within the crystal, which appears owing to the influence of the neighboring atoms (Kara & Kurki-Suonio, 1981) or external and crystal fields in ferromagnetic crystals (Stepanov & Sinha, 2000). These corrections depend on the distortion of the wave functions of external electron shells of the atom (ion) and contribute slightly to $f_0(s)$ but sometimes this contribution can

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† Deceased.

be comparable with the values of f' and f'' (*International Tables for Crystallography*, 1992).

The first result of this paper is a new method for approximating the function $f_0(s)$. Whereas the accuracy and calculation volume of the present technique are comparable with the interpolation method by Cromer & Mann (1968), it also gives directly the approximation for atomic wave functions themselves; this allows ASF to be found in the entire range of arguments taking into consideration the non-sphericity of the atomic shells. The essential feature of a compiled database for the interpolation of wave fuctions is a clear physical meaning of all its fields. The technique for calculation of $f_0(s)$ is based on the operator method (OM) for the approximate solution of the Schrödinger equation (Feranchuk & Komarov, 1982, 1984; Feranchuk *et al.*, 1995).

The second part of the paper deals with the microscopic calculation of the Debye–Waller factor defining a supression of the coherent scattering of X-radiation in a crystal owing to temperature vibrations of nuclei (*International Tables for Crystallography*, 1992). Accurate calculation of the DWF is important for the evaluation of diffraction characteristics, *e.g.* the ratio of integral radiation intensities into different Bragg reflections or angular widths of diffraction peaks (Authier, 1996). The most common way to evaluate the DWF is based on the Debye approximation for the spectrum of acoustical vibrations. This theory utilizes one parameter only, the Debye temperature of the crystal Θ_D, neglecting the anisotropy effects (*International Tables for Crystallography*, 1992). Unfortunately, the values Θ_D are known for a comparatively small number of materials. Besides, even for monoelemental crystals, the Debye temperature depends essentially on the method of experimental measurements. For instance, the data from literature for the Debye temperature in the Ge crystal varies in a very wide range, from 211 to 400 K (*International Tables for Crystallography*, 1992). In the above-mentioned software packages (Brennan & Cowan, 1991; Lugovskaya & Stepanov, 1991), the value of Θ_D for the crystals with a polyatomic unit cell is evaluated by means of an averaging procedure for the Debye temperature of all cell elements. This procedure delivers rather rough estimation for the DWF, despite the argument that the precise value Θ_D is not essential for strong Bragg reflections used in high-resolution X-ray diffraction (HRXRD). As an example, using the data cited in *International Tables for Crystallography* (1992), the susceptibility of X-rays for the reflection 400 in Ge at room temperature and for Cu $K\alpha$ radiation is changing up to 15% within the above-mentioned range of Θ_D, and for the same reflection in Ga the variation reaches almost 50%. Such a large difference can appreciably disfigure the picture of theoretical interpretation of HRXRD spectra. Moreover, for crystals with low symmetry of the unit cell, the DWF is considerably anisotropic (*International Tables for Crystallography*, 1992), and this case should be described by at least three different values of Θ_D. Thus, the development of the method for the theoretical evaluation of the DWF for an arbitrary crystal is an actual problem in HRXRD. The formal connection of the DWF with microscopic characteristics of a phonon spectrum of the crystal is well known (Bruesch, 1987). However, the practical calculation of the DWF requires either the usage of an experimental phonon spectrum (Gao & Peng, 1999) or the solution of a very complicated problem for evaluation of the elements of the harmonic force matrix of the crystal. In the present work, we describe an algorithm for calculating the DWF for crystals taking into account both acoustic and optical branches of the phonon spectrum. The database for elastic force constants of the interaction between arbitrary atoms in the unit cell has been filled. These data are used to calculate the effective Debye temperature as well as the anisotropy of the DWF for crystals.

The paper is structured as follows: in §2, the OM approximation for one-electron wave functions of atoms (ions) is described. The comparison of our results with other known approximations is presented and the procedure for accounting for the non-sphericity of electron density is considered. In §3, these functions are used for the calculation of form factors of free atoms and ions. In §4, the physical structure of a database record for force matrices of crystals is considered and a quantitative estimation for the Debye temperature is derived. The equations for approximate calculation of different branches of the phonon spectrum are derived in §5 and a microscopic estimation of the DWF is discussed taking into account optical phonons and anisotropy factors.

2. The mathematical background

The present work gives a recipe for the creation of a database for ASF using approximated atomic wave functions, which implements the parameters with definite physical sense, in contrast to numerical interpolation by Cromer & Mann (1968). There are papers by Climenti & Raimondi (1963) and by Stewart (1969) and databases where a precise enough analytical approximation for one-electron wave functions has been derived. In most of these cases, the wave functions derived are a result of the numerical interpolation for solutions of the Hartree–Fock equations for free atoms; this makes it difficult to use these functions for a description of a non-spherical electron-density distribution in crystals. Here we use the operator method for the approximate calculation of the atomic wave functions in the crystal. The OM results in the approximate solution for the Schrödinger equation and is valid for the entire range of Hamiltonian parameters. The method has been successfully applied to various quantum systems (Feranchuk & Komarov, 1982, 1984; Feranchuk *et al.*, 1995, 1996). The essential feature of the OM is its locality in the space of eigenstates of the investigated quantum system, *i.e.* a state vector in the zeroth-order approximation includes the variational parameters defined by the condition of 'the best description' of exactly this state. Another important feature is the convergence of the successive approximation of the OM in the entire range of changing of the Hamiltonian parameters. Both these features of the OM have permitted us to find the analytical expression for wave functions of many-electron atoms in crystals using a comparatively small database of parameters with clear physical meaning.

A quantitative description of atomic systems is based on the concept of an independent movement of electrons in a self-consistent field, *e.g.* of a Hartree–Fock potential (Fisher, 1977). One-electron state vectors are considered as a basis for construction of the zeroth approximation for electron wave functions. The OM extends the conception of a common self-consistent field by inclusion of an 'individual' field for every electron in every state. This helps to realize in full measure the idea of the independent movement of electrons, when the total energy of the atom is reduced to the sum of energies of individual electrons; this is in contrast to the total Hartree–Fock energy of an atom, which does not satisfy this condition (Veselov & Labzovskii, 1986). The characteristics of these 'individual' fields are determined by the selection of the basis of one-particle wave functions. For atoms, the most natural basis is generated by functions describing the movement of each electron in its own Coulomb field defined by an effective charge. These individual effective charges are supposed to be different for different electron states and are considered as the OM variational parameters for the best zeroth approximation. The charges are transformed to the charge of an atomic nucleus when the interaction between electrons is adiabatically cut off. The reason for such a parametrization can also be explained by the fact that the Coulomb wave functions with a properly chosen effective charge approximates the Hartree–Fock functions very well (Kregar, 1984).

An individualization of the self-consistent field for the electron in every quantum state does not contradict the permutation symmetry of the initial Hamiltonian of the whole atom. Besides, it is very important to use the basic set of orthonormalized one-electron wave functions for a correct calculation of form factors and higher-order approximations. The construction of an orthonormalized basis starts from the functions $R_{nl}(r, Z_{nl})$, which are the solutions of the radial Schrödinger equation for a particle in the Coulomb field of the charge Z_{nl}, and spherical harmonics $Y_{lm}(\mathbf{n})$. Here, $r = |\mathbf{r}|$; $\mathbf{n} = \mathbf{r}/r$ and n, l, m are the principal, orbital and azimuthal quantum numbers (Landau & Lifshitz, 1963), and atomic units and the traditional spectroscopic classification are used.

Thus, a coordinate part of the wave function of an electron in the first shell is chosen as the $1s$ state in the field with effective charge Z_{1s}:

$$ {}^{1s}\psi(\mathbf{r}, Z_{1s}) = R_{10}(r, Z_{1s})\, Y_{00}(\mathbf{n}). \tag{1} $$

Thus a general form for wave functions of the electron in the second shell is

$$ \begin{aligned} {}^{2s}\psi(\mathbf{r}, Z_{2s}) &= [C_{20}R_{20}(r, Z_{2s}) + C_{21}R_{21}(r, Z_{2s})]Y_{00}(\mathbf{n}), \\ {}^{2p}\psi_m(\mathbf{r}, Z_{2p}) &= R_{21}(r, Z_{2p})\, Y_{1m}(\mathbf{n}). \end{aligned} \tag{2} $$

Here, the coefficients C_{20} and C_{21} are chosen from the conditions of the orthogonality of functions ${}^{1s}\psi$ and ${}^{2s}\psi$ and normalization of the function ${}^{2s}\psi$:

$$ \begin{aligned} \textstyle\int \mathrm{d}\mathbf{r}\, {}^{1s}\psi(\mathbf{r}, Z_{1s})\, {}^{2s}\psi(\mathbf{r}, Z_{2s}) &= 0, \\ \textstyle\int \mathrm{d}\mathbf{r}\, [{}^{2s}\psi(\mathbf{r}, Z_{2s})]^2 &= 1. \end{aligned} \tag{3} $$

This procedure is repeated for the states of electrons in the third shell resulting in the relations:

$$ \begin{aligned} {}^{3s}\psi(\mathbf{r}, Z_{3s}) &= [C_{30}\, R_{30}(r, Z_{3s}) + C_{31}\, R_{31}(r, Z_{3s}) \\ &\quad + C_{32}\, R_{32}(r, Z_{3s})]\, Y_{00}(\mathbf{n}), \\ {}^{3p}\psi_m(\mathbf{r}, Z_{3p}) &= [D_{31}\, R_{31}(r, Z_{3p}) + D_{32}\, R_{32}(r, Z_{3p})]\, Y_{1m}(\mathbf{n}), \\ {}^{3d}\psi_m(\mathbf{r}, Z_{3d}) &= R_{32}(r, Z_{3d})\, Y_{2m}(\mathbf{n}), \end{aligned} \tag{4} $$

where, again, the coefficients C_{30}, C_{31} and C_{32} are defined by the orthogonality of the function ${}^{3s}\psi(\mathbf{r}, Z_{3s})$ to the functions ${}^{1s}\psi(\mathbf{r}, Z_{1s})$ and ${}^{2s}\psi(\mathbf{r}, Z_{2s})$ and by normalization. Coefficients D_{31} and D_{32} can be found from the orthogonality of the functions ${}^{3p}\psi_m(\mathbf{r}, Z_{3p})$ and ${}^{2p}\psi_m(\mathbf{r}, Z_{2p})$ and their normalizations. The formulas above illustrate the procedure for construction of an orthonormalized basis from the Coulomb functions belonging to different effective charges. The set of radial functions with the same principal quantum number n is enough for a similar construction of electron wave functions in any shell. The only free variational parameters in the functions of the OM's zeroth approximation are the effective charges, contrary to the Slater orbitals (Clementi & Roetti, 1974), where essentially more parameters are introduced in order to interpolate the polynomial structure of radial functions.

The reason for constructing the orthonormal basis in this way is also related to the influence the electron kinetic energy operator has on these functions. For example,

$$ \begin{aligned} -\tfrac{1}{2}\Delta\, {}^{1s}\psi(\mathbf{r}, Z_{1s}) &= \left(-\frac{Z_{1s}^2}{2} + \frac{Z_{1s}}{r}\right) {}^{1s}\psi(\mathbf{r}, Z_{1s}) \\ -\tfrac{1}{2}\Delta\, {}^{2s}\psi(\mathbf{r}, Z_{2s}) &= \left(-\frac{Z_{2s}^2}{8} + \frac{Z_{2s}}{r}\right) {}^{2s}\psi(\mathbf{r}, Z_{2s}) \\ &\quad - \frac{C_{21}}{r^2}\, R_{21}(r, Z_{2s})\, Y_{00}(\mathbf{n}). \end{aligned} \tag{5} $$

The components on the right-hand sides of the equations $-(Z_{1s}^2/2)\, {}^{1s}\psi(\mathbf{r}, Z_{1s})$ and $-(Z_{2s}^2/8)\, {}^{2s}\psi(\mathbf{r}, Z_{2s})$ are eliminated when the total Hamiltonian acts on a many-particle wave function. In this case, the result is represented as a sum of one-particle energies of electrons. This one-particle orthonormalized basis along with the effective charges of electrons as free parameters permits the construction of a wave function for the entire atom. For every concrete atomic state, the vector $|\Psi\rangle$ is presented as a sum of antisymmetrized products of one-particle functions from the constructed basis in the form of a Slater determinant (spin functions should be taken into account).

In the zeroth OM approximation (Feranchuk *et al.*, 1995), a diagonal matrix element $E = \langle\Psi|H|\Psi\rangle$ defines the atomic energy with a nuclear charge Z and the Hamiltonian

$$ H = -\tfrac{1}{2}\sum_i \Delta_i - \sum_i Z/r_i + \sum_{i<j} 1/|\mathbf{r}_i - \mathbf{r}_j|. \tag{6} $$

In accordance with the OM (Feranchuk *et al.*, 1995), free parameters (effective charges in our case) can be chosen due to the condition of independence of the diagonal matrix elements of the Hamiltonian in a wave-function representation. In our case, these conditions lead to the equations

$$\frac{\partial E}{\partial Z_{1s}} = 0, \quad \frac{\partial E}{\partial Z_{2s}} = 0, \ldots. \tag{7}$$

Slater's determinant is only considered for the mathematical foundation of the initial approximation. Certainly, the orthonormalization of the basis allows all the advantages of the secondary quantization formalism to be used in routine calculations. Restricting ourselves to completely filled *nl* states for illustrative purposes and introducing the notations

$$e_{nl} = \frac{1}{2l+1} \int \mathrm{d}\mathbf{r} \sum_m [{}^{nl}\psi^*_m(\mathbf{r}, Z_{nl})] \frac{1}{r} [{}^{nl}\psi_m(\mathbf{r}, Z_{nl})], \tag{8}$$

$$ec_{nl} = \frac{1}{2l+1} \int \mathrm{d}\mathbf{r} \sum_m [{}^{nl}\psi^*_m(\mathbf{r}, Z_{nl})] \left(-\tfrac{1}{2}\Delta + \frac{Z^2_{nl}}{2n^2} - \frac{Z_{nl}}{r} \right) \times [{}^{nl}\psi_m(\mathbf{r}, Z_{nl})], \tag{9}$$

$$ee_{n_1l_1n_2l_2} = \frac{1}{(2l_1+1)(2l_2+1)} \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \times \sum_{m_1, m_2} |{}^{n_1l_1}\psi_{m_1}(\mathbf{r}_1, Z_{n_1l_1})|^2 |{}^{n_2l_2}\psi_{m_2}(\mathbf{r}_2, Z_{n_2l_2})|^2, \tag{10}$$

$$\begin{aligned} ex_{n_1l_1n_2l_2} = {} & \frac{1}{(2l_1+1)(2l_2+1)} \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ & \times \sum_{m_1, m_2} [{}^{n_1l_1}\psi^*_{m_1}(\mathbf{r}_1, Z_{n_1l_1})][{}^{n_2l_2}\psi^*_{m_2}(\mathbf{r}_2, Z_{n_1l_1})] \\ & \times [{}^{n_2l_2}\psi_{m_2}(\mathbf{r}_1, Z_{n_2l_2})][{}^{n_1l_1}\psi_{m_1}(\mathbf{r}_2, Z_{n_1l_1})], \end{aligned} \tag{11}$$

the ground-state energy for any atom is given as an algebraic expression. For example, for an atom with four electrons and a nuclear charge *Z*, the energy can be written as (population of the electron states is defined by the Pauli principle)

$$\begin{aligned} E = {} & -2Z^2_{1s}/2 - 2Z^2_{2s}/8 - 2(Z - Z_{1s})e_{10} - 2(Z - Z_{2s})e_{20} \\ & - 2ec_{20} + ee_{1010} + ee_{2020} + 4ee_{1020} - 2ex_{1020}. \end{aligned} \tag{12}$$

The analogous formula for an atom with ten electrons and a nuclear charge *Z* is

$$\begin{aligned} E = {} & -2Z^2_{1s}/2 - 2Z^2_{2s}/8 - 6Z^2_{2p}/8 - 2(Z - Z_{1s})e_{10} \\ & - 2(Z - Z_{2s})e_{20} - 6(Z - Z_{2p})e_{20} - 2e_{20}c + ee_{1010} + ee_{2020} \\ & + 4ee_{1020} + 12ee_{1021} + 12ee_{2021} + 15ee_{2121} - 2ex_{1020} \\ & - 6ex_{1021} - 6ex_{2021} - 6ex_{2121}. \end{aligned} \tag{13}$$

The numerical coefficients in the last formulas are determined by the number of electrons in the occupied states and the number of interacting electron pairs, *i.e.* the number of electron pairs with equally oriented spins contributing to the exchange interaction. According to the formulas (12)–(13), the energy of an atom can be written as a sum of two terms

$$E = E_0 + E_1, \tag{14}$$

where E_0 represents a sum of one-particle energies of electrons, given by the formulas following from the relations (5):

$$E_{1s} = -\frac{Z^2_{1s}}{2}, \quad E_{2s} = -\left(\frac{Z^2_{2s}}{8} + ec_{20} \right), \quad E_{2p} = -\frac{Z^2_{2p}}{8}, \ldots. \tag{15}$$

The value E_1 is the first-order correction of the operator method, caused by an approximate presentation of the potential energy of the atom as a sum of individual potential energies of electrons.

Table 1
Total energies of atoms $E_0 + E_1$ calculated by the OM and E_{HF}, the Hartree–Fock method.

Atom (*Z*)	E_0	E_1	$E = E_0 + E_1$	E_{HF}
Be ($Z = 4$)	−15.4116	0.881635	−14.5300	−14.5730
B ($Z = 5$)	−25.8567	1.40611	−24.4506	−24.5291
F ($Z = 9$)	−104.454	4.57247	−99.8820	−99.4094
Ne ($Z = 10$)	−135.133	5.64220	−129.491	−128.547
Na ($Z = 11$)	−168.803	5.76189	−163.041	−161.859
Mg ($Z = 12$)	−207.919	7.06993	−200.849	−199.615

The results of the OM zeroth approximation can now be juxtaposed with the Hartree–Fock results for some atomic characteristics. Table 1 shows the energies E_0 and E_1 for neutral Be, B, F, Ne, Na and Mg atoms, calculated by assuming the definition of the effective charges as given in (7). Atomic units are used in the calculations and the total Hartree–Fock energy for non-relativistic atoms (Clementi & Roetti, 1974) is presented in the last column. The OM values for the total atomic energy are in a good agreement with the Hartree–Fock method. One of the advantages of the OM approach is the smallness of the non-additive contribution E_1 with respect to the total energy, in contrast to the Hartree–Fock method (Veselov & Labzovskii, 1986). The simple structure of the wave functions used allows the inclusion of a self-consistent relativistic contribution to the atomic Hamiltonian. This requires a renormalization of the effective charges in heavy atoms, which is described below for atomic form factors.

The OM permits successive improvements in the precision of the calculated wave functions by including corrections for non-sphericity of the electron density in external shells. For instance, the procedure to calculate successive corrections by the OM for the crystals with the diamond-type crystallographic unit cell C, Si, Ge is the following. Owing to the influence of the neighbor atoms within the crystal, four external electrons in these atoms have parallel spins and are situated on four normalized tetrahedral orbitals defined by the symmetry of the crystallographic unit cell. These orbitals are as follows (*International Tables for Crystallography*, 1992):

$$\begin{aligned} \psi_1 &= \tfrac{1}{2}[R_{n0}Y_{00} + R_{n1}(-2^{1/2}Y_{11} + Y_{10})]; \\ \psi_2 &= \tfrac{1}{2}[R_{n0}Y_{00} + R_{n1}(2^{1/2}Y_{-11} - Y_{10})]; \\ \psi_3 &= \tfrac{1}{2}[R_{n0}Y_{00} + R_{n1}(-2^{1/2}Y_{-11} - Y_{10})]; \\ \psi_4 &= \tfrac{1}{2}[R_{n0}Y_{00} + R_{n1}(2^{1/2}Y_{11} + Y_{10})]. \end{aligned} \tag{16}$$

Here Y_{lm} are the standard spherical harmonics and R_{nl} are the radial functions of external electrons. These functions are the same as in free atoms but contain other effective charges. The next step is the construction of a determinant based on these ψ_i functions. This determinant describes the four-particle wave function of the atomic external shell and it is used in further calculations of the atomic energy and the ASF variation due to anisotropy of the external shell. These calculations can be made using mono- and two-particle density matrices for electrons in the external shell:

$$\begin{aligned}\rho_1 &= \tfrac{1}{4}[R_{n0}^2 + 3R_{n1}^2],\\ \rho_{12} &= \tfrac{1}{4}[R_{n0}^2(1)R_{n1}^2(2) + R_{n0}^2(2)R_{n1}^2(1)\\ &\quad - 2xR_{n0}(1)R_{n1}(2)R_{n0}(2)R_{n1}(1)\\ &\quad + 2(1-3x^2)R_{n1}^2(1)R_{n1}^2(2)],\end{aligned} \tag{17}$$

where x is the cosine of an angle between vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. These density-matrix expressions are used to find an atom energy and to optimize by means of (7) the effective charge in an external shell of an atom in the crystal. The contribution of the external shell to ASF is calculated as a Fourier image of the density matrix ρ_1. This contribution differs from the analogous density matrix in a free atom,

$$\rho_1^{(0)} = \tfrac{1}{2}[R_{n0}^2 + R_{n1}^2],$$

both in explicit form and due to the renormalized effective charge. Direct physical interpretation of the OM wave functions can be used to find the change in the atomic form factors caused by the external field. For example, in a magnetic field, the atoms C, Si and Ge in their ground states have two external p electrons, which form a state with the total spin $S = 1$ and orbital momentum $L = 1$. Taking the spin–orbital interaction into account, the ground state of these atoms corresponds to the zero eigenvalue of the total momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ (Landau & Lifshitz, 1963). In a magnetic field Ξ, directed along the z axis, the Hamiltonian of the atom is changed by the value

$$\delta H = A(\mathbf{LS}) + \mu_B \Xi (L_z + 2S_z), \tag{18}$$

where $A > 0$ is the constant of the spin–orbit interaction and μ_B is the Bohr magneton. The radial wave functions of the OM zeroth approximation $R_{n1}(r)$, with $n = 2(\mathrm{C}), 3(\mathrm{Si}), 4(\mathrm{Ge})$ do not change but their spin–angular dependence defined by the eigenfunctions of the operator δH can be diagonalized by means of the eigenvectors of the full spin and the momentum operators $|M_L, M_S\rangle$. The ground-state vector of the atom in the field is defined by the following linear combination:

$$\begin{aligned}&|\Phi_0\rangle = c_1|1,-1\rangle + c_2|0,0\rangle + c_3|-1,1\rangle;\\ &c_1 = -\frac{1}{3^{1/2}}(1 + \xi - \tfrac{2}{9}\xi^2), \quad c_2 = \frac{1}{3^{1/2}}(1 - \tfrac{5}{9}\xi^2),\\ &c_3 = -\frac{1}{3^{1/2}}(1 - \xi - \tfrac{2}{9}\xi^2), \quad \xi = \frac{\mu_B \Xi}{A}.\end{aligned} \tag{19}$$

These wave functions lead to the appearance of a non-spherical part in the electron density. As a result, the ASF includes a term proportional to the second Legendre polynomial with an angle θ between the axis z and the vector $\mathbf{q}$. The amplitude of this contribution is defined by an integral of the radial electron density with a Bessel function:

$$\begin{aligned}f_m(\mathbf{q}) &= -\frac{10}{9}\xi^2 P_2(\cos\theta)\int_0^\infty \mathrm{d}r\, r^2 R_{n1}^2(r)\left(\frac{\pi}{2qr}\right)^{1/2} J_{5/2}(qr)\\ &= -\frac{10}{9}\xi^2 P_2(\cos\theta) f_m(s).\end{aligned} \tag{20}$$

Fig. 1 shows the amplitude of the anisotropic part $f_m(s)$ of ASF for Si ($n = 3$) and Ge ($n = 4$) in a magnetic field. It should be noted that the corrections to effective charges of shells are of the second order in magnetic field, therefore the radial functions of a free atom have been used to calculate the integral (20). This amplitude is relatively small in comparison to the isotropic case but for some reflections it can be comparable with the values of anomalous-dispersion corrections. The latter can show up as a new physical effect in X-ray spectra recorded from crystals in rather strong external or intercrystalline magnetic fields. We consider the crystals of silicon and germanium as a simple illustration for the proposed algorithm. The effect of magnetic anisotropy is expected to be more pronounced for atoms of the $3d$ group, but this analysis is out of the scope of the present study.

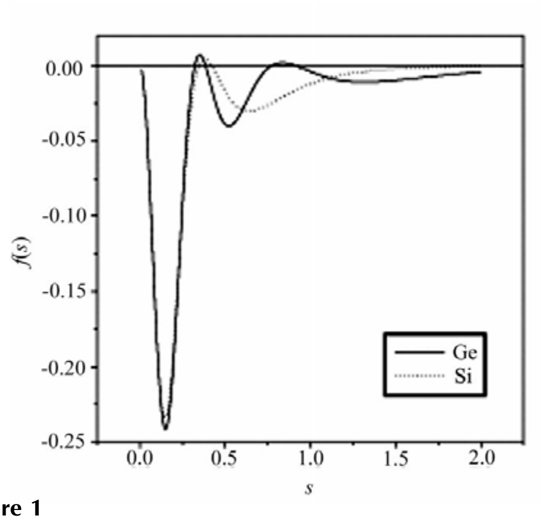

Figure 1
Anisotropic part of ASF in the magnetic field for the atoms of Si (dashed line) and Ge (solid line).

3. Numerical results for the atomic scattering factors

The algorithm for the construction of the atomic wave functions described above has been applied to all atoms in the Periodic Table and most of the ions. Using the basic set of functions from §2, the ASF are represented by algebraic combinations of Fourier images of the Coulomb functions with various effective charges. This has generated a database that includes the set of effective charges for all electron shells of the atoms, obtained along with the populations of the shells for all elements of the Periodic Table and most important ions.[1] The effective charges of electron shells have been calculated taking into account the relativistic corrections to the atomic Hamiltonian. In practical calculations, these parameters can be used for numerical interpolation of form factors (Cromer & Mann, 1968). Certainly, the database is supplemented by the analytical formulas for the partial ASF of each atomic shell, *i.e.* the total ASF of a given atom can be calculated as follows:

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[1] These data are accessible in electronic format and are available from the IUCr electronic archives (Reference: WE0009). Services for accessing these data are described at the back of the journal.

$$f_0(s) = \sum_{n,l} N_{nl} \mathrm{ASF}(nl), \tag{21}$$

where N_{nl} is the population of the electron shell with quantum numbers (n, l) and $\mathrm{ASF}(nl)$ is the partial atomic scattering factor for this shell. Formula (22) contains the analytical expressions $\mathrm{ASF}(nl)$ sufficient for all the atoms and ions of the periodic system of elements.

$$\begin{aligned}
\mathrm{ASF}(1s) &= 16Z_{1s}^4/(s^2+4Z_{1s}^2)^2 \\
\mathrm{ASF}(2s) &= Z_{2s}^4(2s^4-3s^2Z_{2s}^2+Z_{2s}^4)/(s^2+Z_{2s}^2)^4 \\
\mathrm{ASF}(2p) &= (-s^2Z_{2p}^6+Z_{2p}^8)/(s^2+Z_{2p}^2)^4 \\
\mathrm{ASF}(3s) &= 16Z_{3s}^3(19683s^8Z_{3s}-46656s^6Z_{3s}^3+31104s^4Z_{3s}^5 \\
&\quad -5376s^2Z_{3s}^7+256Z_{3s}^9)/(9s^2+4Z_{3s}^2)^6 \\
\mathrm{ASF}(3p) &= 256Z_{3p}^5(-729s^6Z_{3p}+1161s^4Z_{3p}^3-264s^2Z_{3p}^5 \\
&\quad +16Z_{3p}^7)/(9s^2+4Z_{3p}^2)^6 \\
\mathrm{ASF}(3d) &= 256Z_{3d}^7(81s^4Z_{3d}-120s^2Z_{3d}^3+16Z_{3d}^5)/(9s^2+4Z_{3d}^2)^6 \\
\mathrm{ASF}(4s) &= Z_{4s}^4(16384s^{12}-47104s^{10}Z_{4s}^2+42496s^8Z_{4s}^4 \\
&\quad -13760s^6Z_{4s}^6+1744s^4Z_{4s}^8-76s^2Z_{4s}^{10}+Z_{4s}^{12}) \\
&\quad \times(4s^2+Z_{4s}^2)^{-8} \\
\mathrm{ASF}(4p) &= Z_{4p}^6(-10240s^{10}+20480s^8Z_{4p}^2-9024s^6Z_{4p}^4 \\
&\quad +1392s^4Z_{4p}^6-68s^2Z_{4p}^8+Z_{4p}^{10})/(4s^2+Z_{4p}^2)^8 \\
\mathrm{ASF}(4d) &= Z_{4d}^8(1536s^8-2752s^6Z_{4d}^2+784s^4Z_{4d}^4-52s^2Z_{4d}^6 \\
&\quad +Z_{4d}^8)/(4s^2+Z_{4d}^2)^8 \\
\mathrm{ASF}(5s) &= 16Z_{5s}^4(762939453125s^{16}-2441406250000s^{14}Z_{5s}^2 \\
&\quad +2601562500000s^{12}Z_{5s}^4-1130000000000s^{10}Z_{5s}^6 \\
&\quad +223800000000s^8Z_{5s}^8-20416000000s^6Z_{5s}^{10} \\
&\quad +832512000s^4Z_{5s}^{12}-13107200s^2Z_{5s}^{14}+65536Z_{5s}^{16}) \\
&\quad \times(25s^2+4Z_{5s}^2)^{-10} \\
\mathrm{ASF}(5p) &= 256Z_{5p}^6(-30517578125s^{14}+69580078125s^{12}Z_{5p}^2 \\
&\quad -41484375000s^{10}Z_{5p}^4+9943750000s^8Z_{5p}^6 \\
&\quad -1025600000s^6Z_{5p}^8+45792000s^4Z_{5p}^{10} \\
&\quad -768000s^2Z_{5p}^{12}+4096Z_{5p}^{14})/(25s^2+4Z_{5p}^2)^{10} \\
\mathrm{ASF}(5d) &= 256Z_{5d}^8(5126953125s^{12}-10390625000s^{10}Z_{5d}^2 \\
&\quad +4363750000s^8Z_{5d}^4-616800000s^6Z_{5d}^6 \\
&\quad +34272000s^4Z_{5d}^8-665600s^2Z_{5d}^{10}+4096Z_{5d}^{12}) \\
&\quad \times(25s^2+4Z_{5d}^2)^{-10} \\
\mathrm{ASF}(6s) &= Z_{6s}^4(20920706406s^{20}-71672790465s^{18}Z_{6s}^2 \\
&\quad +84845087091s^{16}Z_{6s}^4-43824750624s^{14}Z_{6s}^6 \\
&\quad +11181518640s^{12}Z_{6s}^8-1478114568s^{10}Z_{6s}^{10} \\
&\quad +102614040s^8Z_{6s}^{12}-3642084s^6Z_{6s}^{14}+62046s^4Z_{6s}^{16} \\
&\quad -435s^2Z_{6s}^{18}+Z_{6s}^{20})/(9s^2+Z_{6s}^2)^{12} \\
\mathrm{ASF}(6p) &= Z_{6p}^6(-13559717115s^{18}+33648186915s^{16}Z_{6p}^2 \\
&\quad -23927599584s^{14}Z_{6p}^4+7380652608s^{12}Z_{6p}^6 \\
&\quad -1104924888s^{10}Z_{6p}^8+83875824s^8Z_{6p}^{10} \\
&\quad -3181356s^6Z_{6p}^{12}+57132s^4Z_{6p}^{14}-417s^2Z_{6p}^{16}+Z_{6p}^{18}) \\
&\quad \times(9s^2+Z_{6p}^2)^{-12} \\
\mathrm{ASF}(6d) &= Z_{6d}^8(2410616376s^{16}-5312284236s^{14}Z_{6d}^2 \\
&\quad +2795379660s^{12}Z_{6d}^4-571653369s^{10}Z_{6d}^6 \\
&\quad +53623053s^8Z_{6d}^8-2366334s^6Z_{6d}^{10}+47790s^4Z_{6d}^{12} \\
&\quad -381s^2Z_{6d}^{14}+Z_{6d}^{16})/(9s^2+Z_{6d}^2)^{12} \\
\mathrm{ASF}(7s) &= 16Z_{7s}^4(13410686196639649008 07s^{24} \\
\end{aligned}$$

The analytical expressions for the form factors in the suggested approach are significantly more cumbersome than the conventional combination of the exponents in the mathematical interpolation by Cromer & Mann (1968). They are, however, more flexible owing to their validity for any reflection without limitation of indices. Additionally, they can easily be modified in order to take into account various corrections to ASF (see §2). Fig. 2 shows the atomic scattering factors calculated by the OM (solid lines) and by numerical interpolation by Cromer & Mann (1968) (dots) for atoms Si, Ba and Cu >and ions Mn^{3+} and U^{3+}. The picture demonstrates a good agreement between the two methods in the range $0 < s = \sin\Theta/\lambda < 2$ Å^{-1}.

4. Evaluation of the Debye temperature of crystals

At present, most software packages (Brennan & Cowan, 1991; Lugovskaya & Stepanov, 1991) calculate the Debye–Waller factor on the basis of the Debye model of the phonon spectrum and the phenomenological values of the Debye temperature Θ_D. However, the experimental value of Θ_D is known for relatively few crystals (*International Tables for Crystallography*, 1992) and the averaging procedure for the Θ_D values for a crystal with an unknown experimental Debye temperature is used without a sufficient theoretical justification. Thus, the development of a rigorous method for the evaluation of Θ_D of an arbitrary crystal is a real challenge. Moreover, some diffraction experiments require accurate calulations of the DWF taking into account the anisotropy factors and different branches of the phonon spectrum. The experimental density of the phonon states (Gao & Peng, 1999) are known for only a few materials, whereas the situation is unclear for most crystalline structures. We propose here the method of microscopic simulation of the force matrix for an arbitrary crystal, which helps to realize both the evaluation of Θ_D and the calculation of the DWF with high accuracy.

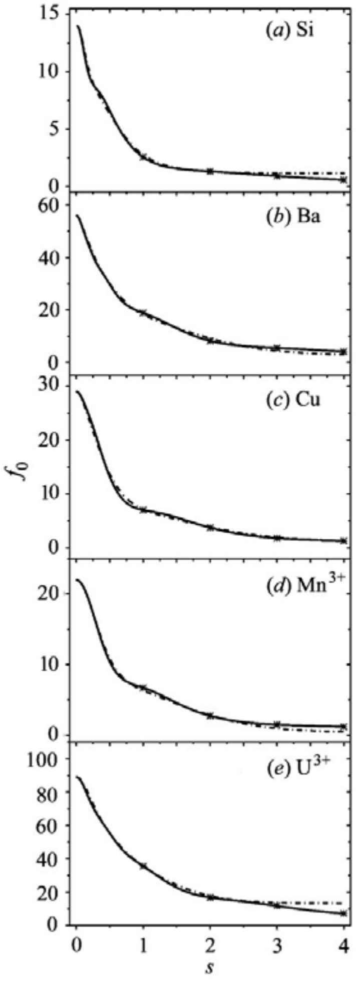

Figure 2
Atomic scattering factor $f_0(s)$ calculated by the OM (solid lines), by numerical interpolation (Cromer & Mann, 1968, dashed lines) and by Hartree–Fock [*CRYSTAL98* (1998), asterisks] for atoms (*a*) Si, (*b*) Ba, (*c*) Cu, and ions (*d*) Mn^{3+} and (*e*) U^{3+}.

If the DWF is parametrized by a single parameter Θ_D, the harmonic oscillations of the atoms in a crystal cell result in an attenuation of the elastic scattering amplitudes by the value of DWF. In the isotropic approximation, this factor for an atom with index p in the crystallographic unit cell is defined by the formula

$$\exp(-2W_p) = \exp[-B_p(T)s^2]. \tag{23}$$

Here, $s = \sin\theta_B/\lambda$ is the transmitted wave vector defined in the standard way. The main contribution to the temperature coefficient $B(T)$ is supposed to be introduced by the acoustic branch of the phonon spectrum, so the result can be presented in the following way (Bruesch, 1987):

$$W_p(T) = \frac{3h^2}{2M_p\kappa_B\Theta}\int_0^1 x\coth\left(\frac{x\Theta}{2T}\right)\mathrm{d}x, \tag{24}$$

where κ_B is the Boltzmann constant and the Debye temperature is defined by the expression

$$\Theta_D = \frac{\hbar u k_D}{\kappa_B}; \qquad k_D = \left(\frac{6\pi^2}{\Omega_0}\right)^{1/3}. \tag{25}$$

This is a result of a linear interpolation of the dispersion law for acoustic phonons $\omega(k) \simeq uk$ within the Debye sphere with radius k_D, which depends on the volume of the unit cell of the crystal Ω_0. Thus, in the considered approximation, the value Θ_D or its related sound velocity u is the only parameter influencing the DWF.

The microscopic parameter u can be found from the dispersion equation for the phonon frequencies defined by the harmonic force matrix of the crystal. Because the approximation of pairwise interactions is satisfactory for the real density of atoms in crystals (Ashcroft & Mermin, 1976), a realistic two-particle potential (Balescu, 1975) can be used for construction of the force matrix. In general, the distance between two neighboring atoms in a crystal differs from the equilibrium distance in the corresponding molecule consisting of the same atoms. However, according to crystallochemical research this difference is small because the atomic binding in the crystals is mainly defined by the same external electron shells as in the molecules (Bokii, 1971). Thus, since a model potential approximates the electron term of two bound atoms in some neighborhood of the equilibrium distance R_0, it can also be used for finding the force matrix elements at distances corresponding to the atom positions within the unit cell of a real crystal. In the approximation of pairwise interaction, the element of the force matrix is defined by the following formula (Ashcroft & Mermin, 1976):

$$D_{ij}^{pq} = \kappa_{pq}\left[\frac{(R_{pq} - R_{0pq})}{R_{pq}}\delta_{ij} + \frac{R_{0pq}}{R_{pq}}n_i^{pq}n_j^{pq}\right]; \quad \mathbf{n}^{pq} = \frac{\mathbf{R}_{pq}}{R_{pq}}. \tag{26}$$

Here, upper indexes in the force matrix enumerate different atoms in the cell and lower ones correspond to atomic shifts from their equilibrium positions in Cartesian coordinates; κ_{pq} and R_{0pq} are the harmonic force constants and the equilibrium distance in the molecule corresponding to the atom pair with indexes (pq), respectively; vector $\mathbf{R}_{pq}$ is the real distance between these atoms in the crystal cell.

In this section, we use the Debye interpolation for the phonon spectrum and neglect the anisotropy effects. This means that the standard dispersion equation for the acoustical phonon branch (Ashcroft & Mermin, 1976) should be averaged over all directions in the space of phonon wave vectors as well as over different directions in the unit cell of the direct space. If the approximation of the nearest neighbors is used for the force matrix of the crystal, the average sound velocity is defined by the following simple formula, which is derived in detail in §5:

$$u = \frac{2\pi c a_0 \bar{\nu}}{3 \times 2^{1/2}}; \quad a_0 = (\Omega_0)^{1/3}; \quad \bar{\nu} = \frac{1}{\sigma}\sum_{p=1}^{\sigma} \nu_{A_pB_p}. \tag{27}$$

Here, a_0 represents the average size of the unit cell; the summation is over all different pairs of nearest-neighbor atoms in the cell, where σ is the number of such a pair; $\nu_{A_pB_p}$ is the oscillation frequency in cm^{-1} for a pair of atoms with the index p; the numerical coefficient 1/3 in (27) is due to averaging over all directions. Substituting (27) into the definition of Debye temperature (25), a universal correlation between Θ_D and $\bar{\nu}$ can be found:

$$\Theta_D = \frac{hc}{3 \times 2^{1/2}\kappa_B}(6\pi^2)^{1/3}\bar{\nu}. \tag{28}$$

The formula (28) corresponds to the known interpretation of the Debye temperature of the crystal; its value is proportional to the characteristic phonon frequency. If a standard unit system is used, the numerical coefficient in (28) is close to unity:

$$\Theta_D\ [K] \simeq \bar{\nu}\ [\mathrm{cm}^{-1}]. \tag{29}$$

If a recipe for the calculation of the harmonic frequency for any given pair of atoms is known then this formula can be used for a simple evaluation of the Debye temperature of an arbitrary crystal. The elastic constant κ_A describing the interaction between the identical atoms in two-atomic homonuclear molecules from one side and the interatomic potential $V(R)$ from other side is expressed as (Huber & Gerzberg, 1979)

$$\begin{aligned} \kappa_A &= (2\pi\nu_A c)^2 M_A, \\ V_A(R) &\simeq -E_0 + \tfrac{1}{2}\kappa_A(R - R_0)^2. \end{aligned} \tag{30}$$

Here the interatomic potential $V(R)$ corresponds to the ground-electron term with the binding energy E_0 at equilibrium distance R_0; ν_A is the principal oscillation frequency of the homonuclear molecule in cm^{-1} composed from two identical atoms with mass M_A; c is the velocity of light. Theoretical *ab initio* calculations of the constant κ_A with a spectroscopic accuracy for homo- and heteronuclear molecules require some complicated quantum-mechanical calculations of electron terms (Gribov & Mushtakova, 1999). However, so-called 'realistic' potentials for atom–atom interaction like the Lennard–Jones potential can provide sufficient accuracy for statistically averaged macroscopic characteristics of molecular gases (Balescu, 1975):

$$V_A(R) = \frac{\beta_A}{R^{12}} - \frac{\alpha_A}{R^6}. \tag{31}$$

The parameter β_A corresponds to the repulsive part of the potential at small distances and the constant α_A is proportional to the product of squared dipole moments of interacting atoms and simulates the van der Waals attraction at large distances (Landau & Lifshitz, 1963). The Lennard–Jones potential does not provide the detailed description of electron terms in the entire range of the interatomic distance (Gribov & Mushtakova, 1999) and therefore it cannot be used for precise evaluation of the dissociation energy of the molecule. Nevertheless, it describes quite well the behavior of real potentials near their minima (Balescu, 1975), which are of special interest for us in the scope of the harmonic approximation. The above-mentioned characteristics of the harmonic potential are expressed through the constants α_A and β_A as

$$R_{0A} = \left[\frac{2\beta_A}{\alpha_A}\right]^{1/6}; \quad E_{0A} = -\frac{\alpha_A^2}{4\beta_A}; \quad \kappa_A = 36\alpha_A\left[\frac{\alpha_A}{2\beta_A}\right]^{4/3}. \tag{32}$$

The temperature factor in structure amplitudes is the result of statistical averaging when the fine details of the potential are not essential. Analogous parametrization by α_A and β_A can then be used to evaluate the Debye temperature for a two-atom potential. Because experimental data received from the cross sections as well as from the oscillation spectra are known for a relatively small set of different atomic pairs, a general recipe for the calculation of α_{AB} and β_{AB} for arbitrary atoms A and B must be provided. Such a general recipe can be derived from the scaling dependence of the interaction potential established in the framework of a statistic theory of atoms (Biersack & Ziegler, 1982). A repulsive part of the potential for two different atoms (ions) has been calculated as a geometric average of interaction potentials $V_A^{(\mathrm{rep})}(R)$ and $V_B^{(\mathrm{rep})}(R)$ taken from independent pairs AA and BB of identical atoms:

Table 2
Parameters of diatomic homonuclear molecules.

Atom	ν (cm^{-1})	E_0 (eV)	R_0 (Å)
H	4401	4.48	0.74
He	1861	2.36	1.04
Be*	1343	13.32	1.39
B	1051	3.02	1.59
C	1854	6.21	1.24
N	2358	9.76	1.10
O	1580	5.12	1.21
F	916	1.60	1.41
Ne	14	0.00	3.10
Na	159	0.72	3.08
Mg	190	0.05	3.89
Al	350	1.55	2.47
Si	510	3.21	2.25
P	780	5.03	1.89
S	726	4.37	1.89
Cl	560	2.48	1.99
Ar	26	0.01	3.76
K	92	0.51	3.90
Ca	241	0.13	4.28
Sc	42	1.65	2.40
Ti*	389	1.30	2.17
V*	452	2.48	2.09
Cr	475	1.56	2.17
Mn	110	0.23	2.59
Fe	318	1.06	2.04
Co	365	1.69	3.20
Ni	386	2.36	2.96
Cu	264	2.03	2.22
Zn*	289	1.78	3.41
Ga*	219	1.40	2.43
Ge*	336	2.82	2.16
As	329	3.96	2.10
Se	430	3.16	2.17
Br	325	1.97	2.28
Kr	24	0.02	4.03
Rb	57	0.49	3.79
Sr*	202	5.82	3.05
Y*	282	1.62	–
Zr*	323	12.05	8.41
Nb	280	11.89	2.36
Mo	370	4.89	–
Tc	–	–	–
Ru*	388	3.41	2.17
Rh*	363	2.92	2.09
Pd*	191	0.73	3.16
Ag	192	1.66	2.59
Cd*	164	0.08	4.28
In	142	1.01	2.86
Sn*	315	1.99	2.78
Sb	242	3.09	2.34
Te	251	2.68	2.56
I	214	1.54	2.66
Xe	30	0.02	4.36
Cs	29	0.39	4.47
Ba*	150	11.26	3.25
La*	197	2.50	2.83
Ce*	886	2.50	2.74
Pr*	240	11.59	–
Nd	–	16.02	–
Pm	–	–	–
Sm	–	7.20	–
Eu*	166	11.43	–
Gd*	216	16.84	–
Tb	248	1.32	–
Dy	–	13.13	–
Ho	251	0.82	3.11
Er	–	14.50	–
Tm	–	6.49	–
Yb	162	0.17	2.89
Lu	246	10.11	2.63
Hf	280	13.11	2.44
Ta	365	13.15	2.36
W	385	9.04	–
Re	290	–	–
Os	260	–	–
Ir	279	6.16	2.36
Pt	218	6.35	2.28
Au	191	2.30	2.47
Hg	36	0.07	3.30
Tl	102	0.90	3.07
Pb	161	0.82	3.03
Bi	156	3.09	3.07
Po	155	1.90	–
Th	249	–	–
U	207	7.61	–

$$V_{AB}^{(\mathrm{rep})}(R)=[V_A^{(\mathrm{rep})}(R)V_B^{(\mathrm{rep})}(R)]^{1/2}. \tag{33}$$

These correlations agree well with the experimental data for a large range of interatomic distances (Biersack & Ziegler, 1982).

Equation (33) allows the evaluation of β_{AB} for interactions between different atoms using the simple formula

$$\beta_{AB}\simeq(\beta_A\beta_B)^{1/2}. \tag{34}$$

A similar correlation can also be justified for other parameters of the potential. Indeed, the potential of attraction becomes essential at larger interatomic distances (Landau & Lifshitz, 1963) and therefore the main contribution to the mutual polarization of atoms is introduced by the small quantity of excited states. Then parameter α_{AB} can be estimated as

$$\alpha_{AB}\simeq[\alpha_A\alpha_B]^{1/2}. \tag{35}$$

Substituting (34) and (35) into (30) and (32), we deduce the combinative rules for the evaluation of potentials for heteronuclear diatomic molecules (the experimental data for the homonuclear molecules are used in this procedure):

$$R_{0AB}=(R_{0A}R_{0B})^{1/2};\quad \nu_{AB}=\left[\nu_A\nu_B\frac{M_A+M_B}{2(M_AM_B)^{1/2}}\right]^{1/2};$$
$$E_{0AB}=(E_{0A}E_{0B})^{1/2};\quad \kappa_{AB}=(2\pi c\nu_{AB})^2\mu_{AB};$$
$$\mu_{AB}=\frac{M_AM_B}{M_A+M_B}. \tag{36}$$

Here ν_A and ν_B are the principal oscillation frequencies of the molecules A_2 and B_2; ν_{AB} corresponds to the molecule AB and the difference in the reduced masses for homo- and heteronuclear molecules is taken into account.

Certainly, these combinative rules are semi-phenomenological owing to the choice of the model potential and because of the lack of a sufficient theoretical ground for the relations (33) and (35). The effectiveness and accuracy of these relations can be investigated by applying them to diatomic molecules with known parameters. Table 2 lists all the necessary parameters for diatomic homonuclear molecules from the reference book by Huber & Gerzberg (1979). The comparison of the calculated binding energy E_0 with the energy of dissociation (Huber & Gerzberg, 1979) is quite formal. This is because the Lennard–Jones potential is not a good model for the electron term for all interatomic distances. In fact, only the parameters ν and R_0 are important for our model since they define the behavior of the potential in the harmonic approximation.

The parameters for molecules marked by the symbol * are absent in Huber & Gerzberg (1979) and we calculated these values by means of our combinative rules based on experimental data for materials containing these atoms along with others.

Figs. 3 and 4 show the comparison of experimental (Huber & Gerzberg, 1979) parameters of heteronuclear molecules with their theoretical values, calculated according to the combinative rules of (36). In these pictures, the x axis represents the experimental values and the y axis the theoretical values. Thus, an ideal correspondence between experiment and theory should result in a situation that all points fall on a single straight line. About 200 different molecules described by Huber & Gerzberg (1979) have been examined. Despite the large variation in the range of absolute values for real molecule parameters, the evaluation of these values using the combinative rules is rather effective: the mean square error is 3% when estimating R_0 and 8% for ν. The largest deviations reach 30% and are related to a few molecules that contain hydrogen, for which the statistical evaluations are not a good approximation. The formula derived can also be used as a rough estimation of the dissociation energy; the mean square error for this parameter is about 25% owing to the above-mentioned reasons. Corrections to the parameters considered for interacting ions can be estimated in the framework of the Tomas–Fermi model (Biersack & Ziegler, 1982).

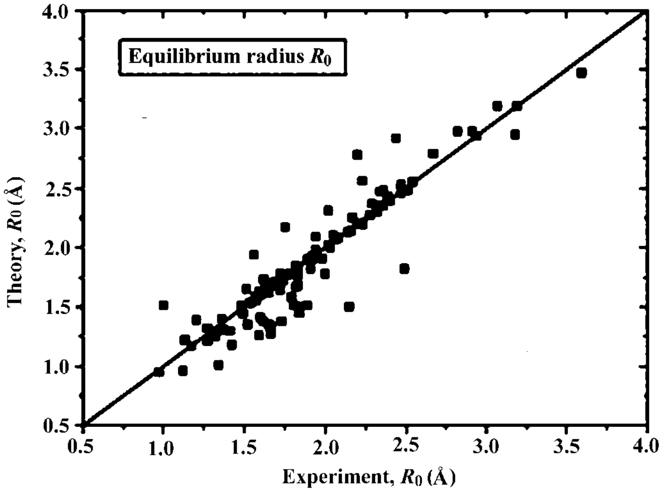

Figure 3
Comparison of the experimental and calculated values of the equilibrium distances R_{AB} for diatomic molecules.

Table 3 gives a comparison between experimental Debye temperatures $\Theta_D^{\rm exp}$ and values calculated with (29). Practically all calculated values of $\Theta_D^{\rm th}$ are within ± 10% of experimentally reported Debye temperatures determined by different methods (*International Tables for Crystallography*, 1992). Fig. 5 is a graphical representation of Table 3 for the coordinates $(\Theta_D^{\rm exp}; \Theta_D^{\rm th})$.

The model Lennard–Jones potential used in this study is not a unique potential for such kinds of calculations. Moreover, the hybridization of external electron shells in crystals can considerably influence the potential (Tsirelson & Ozerov, 1996). Therefore, the combinative formula (36) as well as the approximation of close neighbors in a unit cell have to be considered as a phenomenological rule, the precision of which can be estimated by comparison with experimental data (Table 2, Figs. 3 and 4). The parameters of heteronuclear molecules being combined in other ways, *e.g.* as an arithmetic average, result in worse precision.

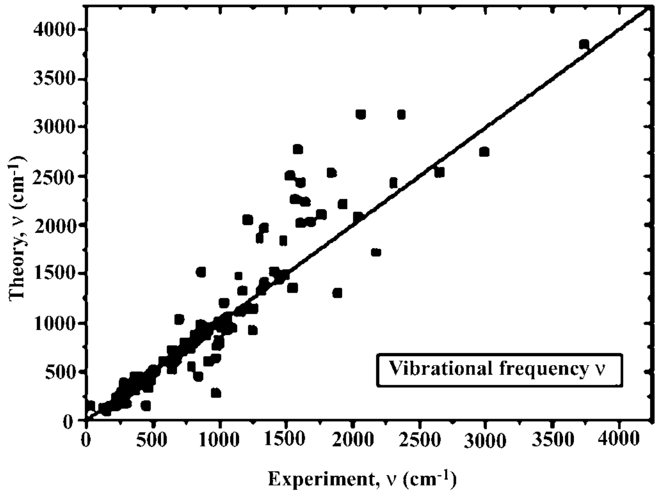

Figure 4
Comparison of the experimental and calculated values of the principal frequencies ν_{AB} for diatomic molecules.

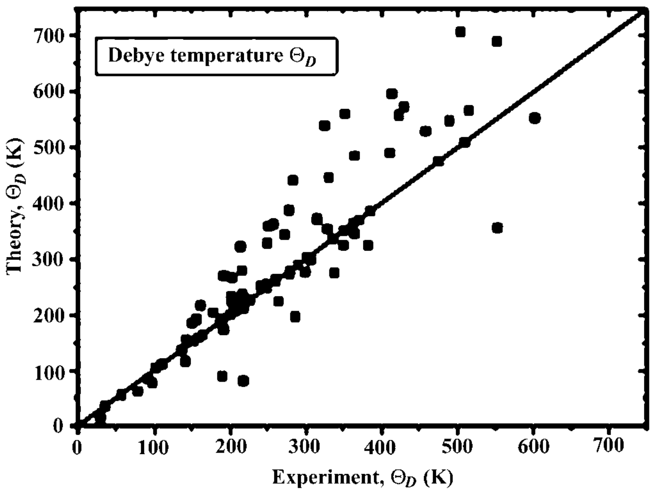

Figure 5
Comparison of the experimental $\Theta_{\rm exp}$ and calculated $\Theta_{\rm th}$ values of the Debye temperatures for crystals.

Table 3
Comparison of the theoretical Θ_{th} and experimental Θ_{exp} Debye temperatures.

Crystal	Cell	$\Theta_D^{\rm exp}$ (K) min	$\Theta_D^{\rm exp}$ (K) max	$\Theta_D^{\rm th}$ (K)	ε
Cu	F.c.c.	304	342	264	0.101
Ag		212	220	192	0.059
Au		155	190	191	0.051
Ca		220	230	241	0.034
Sr		148	171	202	0.118
Al		375	428	350	0.069
Th		145	170	249	0.225
Pb		68	105	161	0.301
V		300	413	452	0.215
Nb		252	301	280	0.006
Ta		230	245	365	0.212
Ni		375	476	386	0.196
Rh		315	370	363	0.029
Pd		263	280	191	0.498
Ir		285	–	279	0.011
Pt		225	248	218	0.041
Li	B.c.c.	277	430	351	0.004
Na		146	180	159	0.012
K		100	163	92	0.177
Rb		58	85	57	0.113
Cs		42	54	29	0.247
Ba		115	–	150	0.132
Cr		405	485	475	0.033
Mo		360	388	370	0.005
W		270	384	385	0.081
Fe		355	467	318	0.307
C	Diamond	1800	2242	1854	0.043
Si		505	685	510	0.077
Ge		211	400	336	0.048
Sn		260	–	315	0.096
Be	H.c.p.	1000	1376	1343	0.061
Mg		290	342	240	0.249
Zn		200	305	289	0.132
Cd		120	172	164	0.058
La		132	152	197	0.288
Gd		152	–	216	0.174
Tl		96	100	102	0.020
Ti		342	430	389	0.118
Zr		250	288	323	0.223
Hf		213	–	280	0.215
Re		275	310	290	0.004
Co		385	–	365	0.027
Ru		400	426	388	0.100
Os		250	256	260	0.014
B	Tetragonal	1250	–	1051	0.086
In		78	129	142	0.157
Sn		163	258	315	0.199
Hg	Rhombohedral	37	100	36	0.311
As		224	285	329	0.255
Sb		140	200	242	0.231
Bi		62	120	156	0.263
U	Orthorhombic	200	–	207	0.017
Ga		125	240	219	0.091
Br		110	–	325	0.494
I		106	–	214	0.338
LiH	*B*1	815	–	1525	0.303
LiF		650	685	602	0.052
LiCl		463	–	515	0.053
LiBr		387	–	458	0.084
LiI		331	–	411	0.108
NaF		439	–	382	0.069
NaCl		270	300	301	0.027
NaBr		200	243	249	0.058
NaI		151	198	217	0.109
KF		321	333	299	0.058
KCl		218	–	227	0.020
KBr		152	–	178	0.079
KI		115	200	152	0.018
RbF		238	–	260	0.044
RbCl		176	–	187	0.030
RbBr		128	–	136	0.030
RbI		108	–	111	0.014
CsF		184	–	200	0.042
AgCl		130	143	352	0.441
PbS		230	–	414	0.286
PbSe		168	–	278	0.247
PbTe		139	–	203	0.187
MgO		750	890	553	0.194
CsCl	*B*2	166	–	141	0.081
CsBr		119	–	98	0.097
CsI		93.6	–	78	0.091
TlCl		125	–	283	0.387
TlBr		114	–	192	0.255
AgI	*B*3	120	183	203	0.145
GaAs		314	–	306	0.013
GaSb		233	–	248	0.031
ZnS		300	–	504	0.254

$\varepsilon_{\rm aver} = 0.135$

5. Algorithm for numerical calculation of the Debye–Waller factor

The method for microscopic simulation of the harmonic potential for an arbitrary pair of atoms presented in the last section allows a more accurate calculation of the DWF. This accuracy is provided by the optical branches of the phonon spectrum and the anisotropy of the DWF in the crystals with a polyatomic unit cell. The anharmonic effects are neglected in this case and the interactions between atoms in neighboring cells are only taken into account when calculating the DWF.

In general, every force matrix element includes four components (Γ, X, Y, Z), which are described as follows:

(Γ): Contribution of the atoms situated in the same unit cell. These elements of the force matrix are denoted by $\Gamma_{i,j}^{\alpha,\beta}$. Here lower indexes correspond to the usual Cartesian components ($i, j = 1, 2, 3$) and upper ones enumerate s atoms in the same cell ($\alpha, \beta = 1, \ldots, s$). The unit cell is assumed to consist of s_1 atoms of one type, s_2 atoms of an other type *etc.*, where $s_1 + s_2 + \ldots = s$. The distance between some atom with number α_1 and all the atoms of the same type in the cell is expressed as

$$R^{11}_{\alpha_1,\beta_1} = \left[\sum_{i=1}^{3}(x_i^{\alpha_1} - x_i^{\beta_1})^2 a_i^2\right]^{1/2},$$

where the dimensionless atom coordinates x_i are measured in fractions of the corresponding basic vectors a_i of the crystal. In the framework of the considered approximation, only the least distances are kept and the number of them defines the coordination number for this type of atom (Ashcroft & Mermin, 1976):

$$l_1, \quad 1 \le l_1 \le s_1, \quad 1 \le \alpha_1 \le s_1, \quad 1 \le \beta_1 \le l_1.$$

The analogous procedure delivers the distances and the coordination numbers for atoms of different types:

$$R^{pq}_{\alpha_p,\beta_q}, \quad 1 \le \alpha_p \le s_p, \quad 1 \le \beta_q \le l_{pq},$$

where l_{pq} is the number of atoms of type q closest to the atom of type p. Then a one-cell contribution to elements of the force matrix is calculated by (26):

$$\Gamma^{\alpha,\beta}_{i,j} \to \Gamma^{\alpha_p,\beta_q}_{i,j} = \kappa_{pq}(x_i^{\alpha_p} - x_i^{\alpha_q})(x_j^{\alpha_p} - x_j^{\alpha_q})a_i a_j [R^{pq}_{\alpha_p,\beta_q}]^{-2}. \tag{37}$$

Here κ_{pq} are the harmonic constants for the interaction between atoms of type p and q, calculated by means of (36).

(X, Y, Z): Three contributions from atoms in neighboring cells. The distances to these atoms can be found by coordinate translations by one of the basis lattice vectors:

$$\begin{aligned}
(XR)^{pq}_{\alpha_p,\beta_q} &= [(x_1^{\alpha_p} - x_1^{\beta_q} - 1)^2 a_1^2 + (x_2^{\alpha_p} - x_2^{\beta_q})^2 a_2^2 \\
&\quad + (x_3^{\alpha_p} - x_3^{\beta_q})^2 a_3^2]^{1/2}, \\
(YR)^{pq}_{\alpha_p,\beta_q} &= [(x_1^{\alpha_p} - x_1^{\beta_q})^2 a_1^2 + (x_2^{\alpha_p} - x_2^{\beta_q} - 1)^2 a_2^2 \\
&\quad + (x_3^{\alpha_p} - x_3^{\beta_q})^2 a_3^2]^{1/2}, \\
(ZR)^{pq}_{\alpha_p,\beta_q} &= [(x_1^{\alpha_p} - x_1^{\beta_q})^2 a_1^2 + (x_2^{\alpha_p} - x_2^{\beta_q})^2 a_2^2 \\
&\quad + (x_3^{\alpha_p} - x_3^{\beta_q} - 1)^2 a_3^2]^{1/2};
\end{aligned}$$

here the same approximation of the nearest neighbors has been used. If the pair of atoms of the selected type has already been encountered in the group Γ of the initial cell, then the same pairs in the groups $(XR), (YR), (ZR)$ are taken into account only when the inequalities $(\square R)^{pq}_{\alpha_p,\beta_q} \le R^{pq}_{\alpha_p,\beta_q}$, $\square = X, Y, Z$, are fulfilled. After such a selection procedure, the additional contributions to the force matrix are calculated as follows:

$$\begin{aligned}
X^{\alpha_p,\beta_q}_{i,j} &= \kappa_{pq}(x_i^{\alpha_p} - x_i^{\alpha_q} - \delta_{i1})(x_j^{\alpha_p} - x_j^{\alpha_q} - \delta_{j1})a_i a_j [(XR)^{pq}_{\alpha_p,\beta_q}]^{-2}; \\
Y^{\alpha_p,\beta_q}_{i,j} &= \kappa_{pq}(x_i^{\alpha_p} - x_i^{\alpha_q} - \delta_{i2})(x_j^{\alpha_p} - x_j^{\alpha_q} - \delta_{j2})a_i a_j [(YR)^{pq}_{\alpha_p,\beta_q}]^{-2}; \\
Z^{\alpha_p,\beta_q}_{i,j} &= \kappa_{pq}(x_i^{\alpha_p} - x_i^{\alpha_q} - \delta_{i3})(x_j^{\alpha_p} - x_j^{\alpha_q} - \delta_{j3})a_i a_j [(ZR)^{pq}_{\alpha_p,\beta_q}]^{-2};
\end{aligned} \tag{38}$$

with δ_{ij} as the Kronecker symbol.

The next step is the calculation of the phonon eigenfrequencies. Taking into account a translational symmetry of the crystal in the equations for small atomic oscillations in the conventional way (Ashcroft & Mermin, 1976), the equations of motion for the phonon variables $\xi_i^{\alpha_p}(\mathbf{k})$ and frequencies are:

$$\begin{aligned}
M_p \omega^2 \xi_i^{\alpha_p} &= \sum_{\beta_q,j} \Gamma^{\alpha_p,\beta_q}_{i,j}(\xi_i^{\alpha_p} - \xi_j^{\beta_q}) \\
&\quad + \tfrac{1}{2}\sum_{\beta_q,j} X^{\alpha_p,\beta_q}_{i,j}(\xi_i^{\alpha_p} - \xi_j^{\beta_q} e^{ik_1 a_1}) \\
&\quad + \tfrac{1}{2}\sum_{\alpha_q,j} X^{\alpha_q,\beta_p}_{i,j}(\xi_i^{\alpha_p} - \xi_j^{\beta_q} e^{-ik_1 a_1}) + \square.
\end{aligned} \tag{39}$$

Here the symbol $\square$ means that the analogous terms with matrices Y, Z should also be included and k_i are the projections of the wave vector on the corresponding basis vectors of the unit cell. We should also note that in general the force matrices in the equations are not symmetrical on all indices. For example, the element X^{α_1,β_q} defines the interaction between an atom of type 1 in the selected cell and atoms of type q in the displaced cell. *Vice versa*, only atoms of type q from the basis cell, which are interacting with an atom of type 1 in the displaced cell, contribute to the element X^{α_q,β_1}.

The approximate solution for (39) is built taking into account the fact that the main contribution in the integrals over the phonon energy in the DWF is defined by the range of small values of k in the vicinity of the extremum of each phonon zone. The principal character of this contribution can be explained by the maximum value of the state density because the phonon group velocity becomes zero in this range (Ashcroft & Mermin, 1976) and the exponentials in (39) can be expanded into the series by k. Besides, the acoustic branches of the phonon spectrum can be extracted by using new variables, namely the coordinate of the center of mass of the cell:

$$R_i = (1/M)\sum_p M_p \sum_{\alpha_p} \xi_i^{\alpha_p},$$

where M is the total mass of the cell; M_p is the mass of the atom of type p, and the relative coordinates are:

$$\rho_i^{\alpha_p} = \xi_i^{\alpha_p} - R_i; \quad \sum_p M_p \sum_{\alpha_p} \rho_i^{\alpha_p} = 0.$$

The last relation means that the number of independent equations is equal to $3(s-1)$ but three other components of the variable (for example, with index $\alpha_p = 1$) depend on the rest and thus can be found from the equation

$$\rho_i^1 = -(1/M_1)\sum_p M_p \sum_{\alpha_p \ne 1} \rho_i^{\alpha_p}. \tag{40}$$

In order to find the motion equation for the center of mass, all the equations (39) are summarized by justifying to an accuracy $O(k^2)$:

$$\begin{aligned}
M\omega^2 R_i &= \frac{k_1^2 a_1^2}{2}\sum_p \sum_{\alpha_p} \sum_{\beta_q,j} [X^{\alpha_p,\beta_q}_{i,j} + X^{\alpha_q,\beta_p}_{i,j}] R_j \\
&\quad + \frac{ik_1 a_1}{2}\sum_p \sum_{\alpha_p} \sum_{\beta_q,j} [X^{\alpha_p,\beta_q}_{i,j} - X^{\alpha_q,\beta_p}_{i,j}] \rho_j^{\beta_q} + \square.
\end{aligned} \tag{41}$$

The equations for the relative variables can be solved in the approximation of the independent oscillations, which is also used in the theory of small vibrations of molecules (Gribov & Mushtakova, 1999). In this case, the coupling of various oscillations is taken into account only through the coordinate of the mass center. Then the average deviation of each atom from its equilibrium position is equal to zero relative to the center of mass of the unit cell. From this fact, the equations of motion for relative coordinates are as follows:

$$\begin{aligned}
M_p \omega^2 \rho_i^{\alpha_p} &= -M_p \omega^2 R_i + \sum_{\beta_q,j} [\Gamma^{\alpha_p,\beta_q}_{i,j} + \tfrac{1}{2}(X^{\alpha_p,\beta_q}_{i,j} + X^{\alpha_q,\beta_p}_{i,j})] \rho_j^{\alpha_p} \\
&\quad - \frac{ik_1 a_1}{2}\sum_{\beta_q,j} [X^{\alpha_p,\beta_q}_{i,j} - X^{\alpha_q,\beta_p}_{i,j}] R_j + \square.
\end{aligned} \tag{42}$$

Physically, the approximation used means that only the average force acting on the selected atom from the side of all neighbors is taken into account. For the case of small k, the optical frequencies $\omega_p^{(\nu)}$, $\nu = 1, 2, 3$, can be found from (42).

The number of such optical branches is $3(s-1)$ and for atoms of the type p they are degenerate with multiplicity $3s_p$ [for the first one the multiplicity is $3(s_1-1)$]. These branches of the phonon spectrum are defined by diagonalization of p matrices of dimension 3×3, which result in the following equations for the eigenfrequencies and orthonormalized polarization vectors $e_i^\nu(p)$:

$$\begin{aligned} &\omega_p^{(\nu)} = (\lambda_p^\nu / M_p)^{1/2}; \quad \lambda_p^\nu e_i^\nu = \sum_j D_{ij}^p e_j^\nu; \\ &D_{ij}^p = \sum_{\beta_q, j} [\Gamma_{i,j}^{\alpha_p,\beta_q} + \tfrac{1}{2}(X_{i,j}^{\alpha_p,\beta_q} + X_{i,j}^{\alpha_q,\beta_p}) + \square]. \end{aligned} \tag{43}$$

The acoustic branches can then be found from (41) by substitution of the relative coordinates by the center of mass. Then the spectrum of the acoustic eigenfrequencies is defined by the acoustic four-rank tensor depending on the force matrix and the vector $\mathbf{k}$ (Landau & Lifshitz, 1987). As a result, there exists an anisotropy of the sound velocity in different directions of propagation even in cubic crystals. However, by definition, the DWF depends on the constant two-rank tensor which is determined by the symmetry of the crystal only and does not depend on the vector $\mathbf{k}$ (Landau & Lifshitz, 1987) because of the averaging over $\mathbf{k}$ during the integration on the phonon variables. This fact allows the use of an averaging procedure over all the directions of $\mathbf{k}$ in the dispersion equation. Mathematically, this corresponds to the following substitution:

$$\begin{aligned} &\textstyle\int f[\omega(\mathbf{k})] k^2 \, \mathrm{d}k \, \mathrm{d}\Omega \simeq \int f[\langle \omega(k) \rangle] k^2 \, \mathrm{d}k \, \mathrm{d}\Omega, \\ &\langle \omega(k) \rangle = I^{1/2}; \quad I = (1/4\pi) \textstyle\int \omega^2(\mathbf{k}) \, \mathrm{d}\Omega. \end{aligned}$$

Then (41) transforms to:

$$\begin{aligned} M\omega^2 R_i = {} & \frac{k^2 a_1^2}{6} \sum_p \sum_{\alpha_p} \sum_{\beta_q, j} [X_{i,j}^{\alpha_p,\beta_q} + X_{i,j}^{\alpha_q,\beta_p}] R_j \\ & + \frac{k^2 a_1^2}{12 M_1} \sum_q M_q \sum_{\alpha_p} \sum_{\beta_q \neq 1, m} [X_{i,m}^{\alpha_p,1} - X_{i,m}^{1,\beta_p}] \\ & \times \sum_{\gamma_r, l} [D_{ml}^q]^{-1} \sum_j [X_{l,j}^{\beta_q,\gamma_r} - X_{l,j}^{\beta_r,\gamma_q}] R_j \\ & - \frac{k^2 a_1^2}{12} \sum_p \sum_{\alpha_p \neq 1} \sum_{\beta_q, m} [X_{i,m}^{\alpha_p,\beta_q} - X_{i,m}^{\alpha_q,\beta_p}] \\ & \times \sum_{\gamma_r, l} [D_{ml}^q]^{-1} \sum_j [X_{l,j}^{\beta_q,\gamma_r} - X_{l,j}^{\beta_r,\gamma_q}] R_j + \square \end{aligned} \tag{44}$$

and the problem is again reduced to the diagonalization of the symmetrical 3×3 matrix. The solution for optical frequencies is then found in the form

$$\omega_a^\nu(k) = (k a_0 / M^{1/2}) c_\nu, \quad \nu = 1, 2, 3, \quad a_0 = (\Omega_0)^{1/3},$$

and defines three acoustical phonon branches. In this parametrization, the normalized vectors of polarization e_{ia}^ν and eigenvalues c_ν no longer depend on k:

$$\begin{aligned} c_\nu^2 e_{ia}^\nu = {} & \sum_j A_{ij} e_{ja}^\nu; \\ A_{ij} = {} & \frac{b_1^2}{6} \sum_p \sum_{\alpha_p} \sum_{\beta_q, j} [X_{i,j}^{\alpha_p,\beta_q} + X_{i,j}^{\alpha_q,\beta_p}] \\ & + \frac{b_1^2}{12} \sum_q M_q \sum_{\alpha_p} \sum_{\beta_q \neq 1, m} [X_{i,m}^{\alpha_p,1} - X_{i,m}^{1,\beta_p}] \\ & \times \sum_{\gamma_r, l} [D_{ml}^q]^{-1} \sum_j [X_{l,j}^{\beta_q,\gamma_r} - X_{l,j}^{\beta_r,\gamma_q}] R_j \\ & - \frac{k^2 b_1^2}{12} \sum_p \sum_{\alpha_p \neq 1} \sum_{\beta_q, m} [X_{i,m}^{\alpha_p,\beta_q} - X_{i,m}^{\alpha_q,\beta_p}] \\ & \times \sum_{\gamma_r, l} [D_{ml}^q]^{-1} \sum_j [X_{l,j}^{\beta_q,\gamma_r} - X_{l,j}^{\beta_r,\gamma_q}] + \square; \\ b_i = {} & \frac{a_i}{a_0}. \end{aligned} \tag{45}$$

To derive a final formula for the DWF, the general definition of the DWF is used for the atom with number t in the unit cell (*International Tables for Crystallography*, 1992):

$$\mathrm{DWF}_t = \exp\left(-\sum_{i,j} B_{ij}^t q_i q_j \right), \quad B_{i,j}^t = 2 \frac{\hbar^2}{M_t} W_{i,j}. \tag{46}$$

Here the projections of the transmitted wave vector q_i should be calculated in the coordinate system connected with unit cell

$$q_i = (2\pi / d l_i), \quad d = (l_1^2 g_1^2 + l_2^2 g_2^2 + l_3^2 g_3^2)^{-1/2},$$

where d is the interplanar distance for the given reflection defined by Miller indices l_i; n_i are the minimal integers for this reflection; $\mathbf{g}_i$ are the standard basis vectors of the reciprocal lattice. In this definition, tensor W_{ij} does not depend on the atom number and is the characteristic of the crystal as a whole (Bruesch, 1987):

$$W_{ij} = \frac{\Omega_0}{2\hbar} \sum_{(p)} \sum_\nu e_i^\nu e_j^\nu \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} f(\omega_p^\nu), \tag{47}$$

where the summation is performed on all optical and acoustic branches and f is the function of the Bose–Einstein distribution

$$f(\omega) = \frac{1}{\omega} \left[1 + \frac{2}{\exp \hbar\omega / k_B T - 1} \right].$$

Below we split the general expression for W into two parts related to optical W^o and to acoustic W^a oscillations. The above-mentioned expansion on small k corresponds to the Einstein approximation when the optical frequencies are considered as constants in the Brillouin zone (Ashcroft & Mermin, 1976). Then taking into account the multiplicity of the optical branches, W^o is calculated as

$$W_{ij}^o = \frac{1}{2\hbar} \sum_p s_p' \sum_\nu e_i^{\nu p} e_j^{\nu p} f(\omega_p^\nu). \tag{48}$$

The frequencies and vectors of polarization for optical branches have been defined in (43). Index s_p' means that the value $(s_1 - 1)$ should be substituted instead of s_1 for the atoms of type 1. The acoustic contribution to the DWF can be found in the following form:

$$W^a_{ij} = \frac{1}{2\hbar}\sum_\nu e^\nu_{ia} e^\nu_{ja} \frac{\Omega_0}{2\pi^2}\int_0^{k_D} \mathrm{d}k\, \frac{kM^{1/2}}{a_0 c_\nu} \times [1 + 2(\exp \hbar k a_0 c_\nu / k_B T M^{1/2} - 1)^{-1}];$$

$$k_D = \left(\frac{6\pi^2}{\Omega_0}\right)^{1/3}. \qquad (49)$$

In analogy to the Debye temperature, three different parameters are introduced for each polarization of the acoustic phonons:

$$\Theta_\nu = \frac{\hbar a_0 k_D c_\nu}{k_B M^{1/2}},$$

and finally the acoustic part of the DWF is

$$W^a_{ij} = \frac{3}{2k_B}\sum_\nu e^\nu_{ia} e^\nu_{ja} \frac{1}{\Theta_\nu}\int_0^1 x\, \mathrm{d}x \coth\left(\frac{x\Theta_\nu}{2T}\right). \qquad (50)$$

The formulas (48), (49), (50) form the basis of the algorithm for calculation of the Debye–Waller factor in the X-ray susceptibilities. By this algorithm, the Fourier components of the susceptibility of crystals are calculated by using the symmetrical tensor W, which includes only six components in the most general case. To illustrate this result, the Debye–Waller factors for the atoms of As and Ga in the crystal GaAs have been calculated. Fig. 6 demonstrates a good agreement between the DWF temperature dependence calculated by the proposed method and the phenomenological dependence found on the basis of the experimental density of the phonon states (Gao & Peng, 1999). The optical part of the DWF, usually not taken into account in the standard program packages (Brennan & Cowan, 1991; Lugovskaya & Stepanov, 1991), seems to be an important part of the total DWF value, as Fig. 6 illustrates.

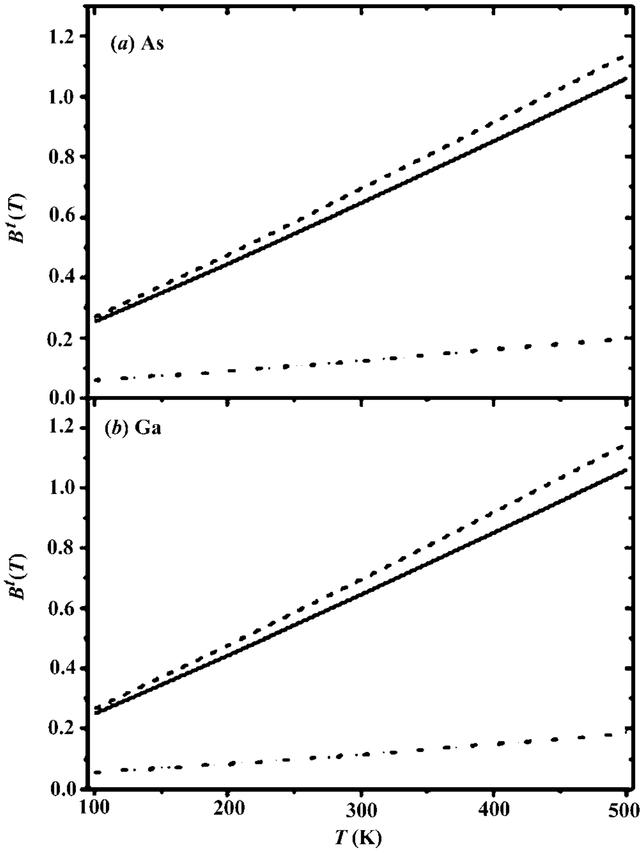

Figure 6
The value $B^t(T)$ in the Debye–Waller factor for the atoms of (*a*) As and (*b*) Ga in the crystal GaAs ($\Theta_D = 210$ K) as a function of the temperature. The dashed line presents the results of Gao & Peng (1999), obtained on the basis of an experimental phonon spectrum; the solid line is a calculation by the present algorithm; the dash–dotted curve represents the optical phonon branch.

6. Summary

In the present work, the concept is presented for further improvement of existing calculation methods for X-ray susceptibility of crystals. This concept contains three principal directions: (i) calculation of atomic form factors taking into account the influence of the atom's surroundings; (ii) an algorithm for calculation of Debye temperature for the crystals with polyatomic unit cell; (iii) method for microscopical calculation of the Debye–Waller factor including different branches of the phonon spectrum. Illustrative examples are presented for using this concept for application to some known crystallographic structures. In forthcoming studies, we plan further detailed testing of the presented concept applied to different problems of high-resolution X-ray diffraction.

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addenda and errata

A new method for calculation of crystal susceptibilities for X-ray diffraction at arbitrary wavelength. Erratum

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In the paper by Feranchuk, Gurskii, Komarov, Lugovskaya, Burgäzy & Ulyanenkov [*Acta Cryst.* (2002). A**58**, 370–384], there is a misprint in equation (22): instead of parameter s, the normalized parameter $s_1 = 4\pi a_0 s$ has to be used, where $a_0 =$ 0.529177 Å is a Bohr radius. The conclusions and other results are correct.

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† Deceased.