

Symmetrical Cases of Simultaneous X-ray Diffraction and the Borrmann Effect. I. The Analysis of Photoelectric Absorption

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The strong enhancement of the anomalous transmission (Borrmann) effect in the symmetrical cases of simultaneous diffraction of three, four and six waves is considered. The analytical solution of the diffraction problem has been obtained when the Bragg conditions are satisfied exactly. The effect of the suppression of photoelectric absorption is investigated with consideration of both dipole and quadrupole interactions.

I. Introduction

Eleven years ago Borrmann & Hartwig (1965) discovered the new effect that anomalous transmission is strongly enhanced when the incident beam of X-rays is diffracted on two systems of planes of the germanium crystal, (111) and (11 $\bar{1}$), simultaneously as compared with the case of diffraction on the system of planes (111) only. This paper stimulated interest in the dynamical theory of simultaneous X-ray diffraction. The detailed theoretical analysis of the case investigated by Borrmann & Hartwig (1965) was done by Hildebrandt (1967). It turned out that the wave field formed in the crystal by three-wave diffraction was such that the points of minimum energy density coincided with the atomic equilibrium positions. In the two-wave case of diffraction by the system of planes (111) the ratio of the local energy of the field to a mean value at a node of the crystal lattice is $(1 - 1/\sqrt{2})$ and therefore considerable interaction between the field of X-rays and the atomic electrons takes place.

Later, anomalous-transmission enhancement of this type was observed time and again by other authors. The more interesting question is, however, the enhancement of the anomalous-transmission effect as compared with the two-wave case for planes (220) when the wave field formed has nodes just at the crystal lattice sites. The attempts to discover this effect by means of experimental methods gave no positive results for a long time. However, Joko & Fukuhara (1967) had shown theoretically that in the symmetrical four-wave and, particularly, six-wave cases this enhancement must exist. An attempt to directly confirm the Joko & Fukuhara (1967) result had been undertaken by Huang, Tillinger & Post (1973), however, without success. The first qualitative confirmation of the theory had been obtained, apparently, by Kshevet-skii & Myhailjuk (1976).

In this paper we give a more detailed analysis than Joko & Fukuhara (1967) of the Borrmann effect in the symmetrical cases of simultaneous diffraction. For the sake of simplicity we restrict our treatment to the

case of photoelectric absorption, which is the main contribution to the normal absorption coefficient μ_0 . An analysis of the absorption due to thermal and Compton scattering processes will be given in a separate paper.

II. Formulation and solution of the diffraction problem

To describe the electromagnetic field of X-rays inside a crystal, we use Maxwell's equations. In terms of space and time Fourier components of the electrical field vector, $\mathbf{E}(\mathbf{k}, \omega)$,

$$(\mathbf{k}^2 - \kappa^2)\mathbf{E}(\mathbf{k}, \omega) - \mathbf{k}[\mathbf{k}\mathbf{E}(\mathbf{k}, \omega)] = \frac{4\pi i\omega}{c^2} \mathbf{j}(\mathbf{k}, \omega) \quad (2.1)$$

where $\kappa = \omega/c$, c is the light velocity, $\mathbf{j}(\mathbf{k}, \omega)$ is the Fourier component of the current density, which in fact is a quantum-mechanical average of the Fourier component of the current-density operator. In the linear approximation in E , taking into account the periodicity of the crystal lattice, we have

$$\frac{4\pi i\omega}{c^2} \mathbf{j}(\mathbf{k}, \omega) = \kappa^2 \sum_m \chi^{il}(\mathbf{k}, \mathbf{k}_m) \mathbf{E}^l(\mathbf{k}_m, \omega) \quad (2.2)$$

where $\mathbf{k}_m = \mathbf{k} + \mathbf{h}_m$, \mathbf{h}_m is 2π times the reciprocal-lattice vector, $\chi^{il}(\mathbf{k}, \mathbf{k}_1)$ is 4π times the Fourier component of the polarizability tensor of the crystal.

The expression for $\chi^{il}(\mathbf{k}, \mathbf{k}_1)$, which takes into account all possible interactions between the X-rays and the crystal, has been obtained by Afanas'ev & Kagan (1968). The real part of the polarizability is determined mainly by the Thomson scattering of X-rays by the electrons of the atoms. It has the form:

$$\begin{aligned} \chi_r^{il}(\mathbf{k} - \mathbf{k}_1) &= -\delta^{il} \frac{4\pi r_0}{\kappa^2 \Omega_0} \\ &\times \sum_j \exp[-i(\mathbf{k} - \mathbf{k}_1)\mathbf{q}_j] f_j(\mathbf{k} - \mathbf{k}_1) \exp[-W_j(\mathbf{k} - \mathbf{k}_1)]. \end{aligned} \quad (2.3)$$

Here the summation is over all the atoms in the unit cell of a crystal, $\exp(-W_j)$ and f_j are the Debye-

Waller factor and the Fourier component of the electron density (form factor) of the j atom, Ω_0 is the volume of a unit cell, $r_0 = e^2/mc^2$.

To calculate the photoelectric-absorption contribution to the imaginary part of the polarizability one usually uses the multipole series (Hildebrandt, Stephenson & Wagenfeld, 1973). It is enough to retain only the dipole and quadrupole terms because the remaining terms are small; then we have

$$\chi_i^{il}(\mathbf{k}, \mathbf{k}_1) = \chi_i^D(\mathbf{k} - \mathbf{k}_1)\delta^{il} + \chi_i^Q(\mathbf{k} - \mathbf{k}_1) \left[\delta^{il} \frac{(\mathbf{k}\mathbf{k}_1)}{\kappa^2} + \frac{k_1^i k_1^l}{\kappa^2} \right] \quad (2.4)$$

where

$$\chi_i^{D,Q}(\mathbf{k}) = \frac{1}{\kappa\Omega_0} \sum_j \exp(-i\mathbf{k}\mathbf{Q}_j) \sigma_j^{D,Q} \exp[-W_j(\mathbf{k})] \quad (2.5)$$

and $\sigma_j^{D,Q}$ are the cross-sections of dipole and quadrupole photoabsorptions of the atom j . The dipole term of the imaginary part of the polarizability as well as the real part is diagonal in the vector indices. It is convenient to introduce the complex quantity $\chi^D = \chi_r^D + i\chi_i^D$, where χ_r^D is defined by (2.3). We note that for X-rays

$$|\chi_r^D| \gg |\chi_i^D| \gg |\chi_i^Q|. \quad (2.6)$$

Let us consider the usual case where the plane wave with wave vector $\mathbf{\kappa}$ falls on a crystal in the form of a plate. The crystal is cut and orientated in such a way that the Bragg condition, $(\mathbf{\kappa} + \mathbf{h}_m)^2 = \kappa^2$, is satisfied for the several reciprocal lattice vectors simultaneously. Let these vectors lie in the same plane, which is parallel to the entrance surface of a crystal, and form a regular polygon. In a crystal of cubic symmetry, reciprocal-lattice vector combinations in the form of an equilateral triangle, a square and a regular hexagon can occur with the number of strong waves, N , equal to 3, 4 and 6. At a vacuum-crystal boundary the plane wave is refracted and the vector $\mathbf{\kappa}$ is transformed by $\mathbf{\kappa}_0 = \mathbf{\kappa} + \kappa\epsilon_0\mathbf{n}_0/\cos\theta$; where \mathbf{n}_0 is the inner normal to the entrance surface of the plate, $\cos\theta = (\mathbf{s}_m\mathbf{n}_0)$, \mathbf{s}_m is the unit vector parallel to $\mathbf{k}_m = \mathbf{k}_0 + \mathbf{h}_m$ and ϵ_0 is a small quantity of the order of χ ; the imaginary part of which determines the interference absorption coefficient along vector $\mathbf{\kappa}$:

$$\mu^{(N)} = 2\kappa\epsilon_0. \quad (2.7)$$

After the substitution of (2.2) in (2.1) we retain only strong waves and obtain the set of N vector equations. Generally speaking, the transverse character of X-rays inside the crystal is not conserved. However, the longitudinal components are a factor of $\chi \sim 10^{-5}$ smaller than the transverse ones, and they may be neglected. Let us introduce, following Joko & Fukuhara (1967), unit vectors of polarization, $\mathbf{e}_{m\pi}$ and $\mathbf{e}_{m\sigma}$, which form together with \mathbf{s}_m a right-handed system of

orthogonal directions for each reciprocal point m . The vectors $\mathbf{e}_{m\sigma}$ lie in the same plane as the vectors \mathbf{h}_m and $(\mathbf{e}_{m\pi}\mathbf{n}_0) < 0$. Expanding each vector $\mathbf{E}(\mathbf{k}_m)$ in terms of the polarization vectors,

$$\mathbf{E}(\mathbf{k}_m) = E_{m\pi}\mathbf{e}_{m\pi} + E_{m\sigma}\mathbf{e}_{m\sigma}, \quad (2.8)$$

it is easy to obtain the set of linear homogeneous equations for amplitude E_{ms} , $s = \pi, \sigma$, in the form:

$$\sum_{ns'} g_{mn}^{ss'} E_{ns'} = \epsilon_0 E_{ms} \quad (2.9)$$

where

$$g_{mn}^{ss'} = \frac{1}{2} \{ \chi^D(\mathbf{h}_{m-n})(\mathbf{e}_{ms}\mathbf{e}_{ns'}) + i\chi_i^Q(\mathbf{h}_{m-n})[(\mathbf{e}_{ms}\mathbf{e}_{ns'}) (\mathbf{s}_m\mathbf{s}_n) + (\mathbf{e}_{ms}\mathbf{s}_n)(\mathbf{e}_{ns'}\mathbf{s}_m)] \}. \quad (2.10)$$

Thus the interference absorption coefficients (2.7) and the shape of the electric field inside the crystal are determined from the solution of the eigenvalue problem of the scattering matrix $g_{mn}^{ss'}$.

We note that the condition $\exp(i\mathbf{h}_m\mathbf{Q}_j) = 1$ is satisfied for all atoms j in the unit cell and all the reciprocal-lattice vectors \mathbf{h}_m in the symmetrical cases. Then the scattering matrix has such symmetrical properties as the many-wave pyramid. It is easy to obtain the general form of its eigenvectors from analysis of the symmetrical properties of the pyramid.

Considering index m as the integer variable, we easily find that the substitution $m' = m + 1$ instead of m is equivalent to the rotation of the reciprocal-lattice vector polygon by an angle $2\pi/N$. The substitution $m' = m + N$ instead of m leads to the identical transformation of the polygon. Therefore we have the cyclic condition $E_{m+N, s} = E_{ms}$ for the amplitudes E_{ms} and its linear independent solutions read

$$E_{ms} \sim \sin\left(\frac{2\pi n}{N} m\right); \cos\left(\frac{2\pi n}{N} m\right)$$

where n is the integer divisor of $N = 3, 4, 6$.

The index s takes two values and, consequently, the amplitudes E_{ms} can be formally represented as four combinations of sines and cosines. To choose the correct ones we consider the refraction transformation in the plane x , which is perpendicular to the plane of the reciprocal-lattice vectors and coincides with the point o and the centre of the circumscribed circle. Then the projection of the electric-field vector on the plane at the lattice sites,

$$E^x \sim \sum_m (E_{m\pi} e_{m\pi}^x + E_{m\sigma} e_{m\sigma}^x),$$

either does not change or changes sign. On the other hand this operation is equivalent to the substitution $m' = N - m$ instead of m . Because $e_{m'\pi}^x = e_{m\pi}^x$, $e_{m'\sigma}^x = -e_{m\sigma}^x$, the amplitudes must have analogous properties. Consequently only the following combinations are possible:

$$\begin{aligned}
(n\pi): E_{m\pi} &= A \cos\left(\frac{2\pi n}{N} m\right), E_{m\sigma} = -B \sin\left(\frac{2\pi n}{N} m\right) \\
(n\sigma): E_{m\pi} &= A \sin\left(\frac{2\pi n}{N} m\right), E_{m\sigma} = B \cos\left(\frac{2\pi n}{N} m\right)
\end{aligned} \tag{2.11}$$

and only the coefficients A and B remain undetermined. In fact, it is enough to determine only the ratio A/B because the coefficients can then be determined from the normalization condition.

It is easily found that for the solution $(n\pi)$ with $n=N$ all the σ components of the field are equal to zero, and the π components are equal to one another. When $n=N/2$ (if N is even) all the σ components also are zero, and the π components in turn change sign (antisymmetrical solution). In these cases $A=1/\sqrt{N}$. Similarly with the solutions $(n\sigma)$ with $n=N, N/2$ where $B=1/\sqrt{N}$. All these solutions correspond to a non-degenerate eigenvalue ε_0 , which is obtained after substitution of (2.11) into any equation of the set (2.9). On the other hand, the solutions $(n\pi)$ and $(n\sigma)$ for $n \neq N, N/2$ correspond to a doubly degenerate eigenvalue because the symmetry transformation equalizes them. On substituting any solution (2.11) in any two equations of the set (2.9), we obtain the set of two linear equations for finding ε_0 and A/B . Here there are two values for ε_0 for a given value n , which we shall mark by $(n\pi, \sigma \pm)$. It is convenient to use the following expressions for the coefficients A and B of this solution:

$$A_{\pm} = -\sqrt{\frac{2}{N}} \frac{Z_{\pm}}{\sqrt{(1+Z_{\pm}^2)}}, B_{\pm} = \sqrt{\frac{2}{N}} \frac{1}{\sqrt{(1+Z_{\pm}^2)}} \tag{2.12}$$

where $Z_{\pm} = \xi \pm \sqrt{1+\xi^2}$, and the quantity ξ is determined from the set simultaneous with ε_0 .

Taking into consideration the inequality (2.6), we can use only the real part of the scattering matrix to find ξ and ε_0 , so that the eigenvectors are real. After that, the interference absorption coefficients are determined by the formula, to the term in first-order, of the perturbation theory:

$$\mu^{(j)} = 2\kappa \sum_{\substack{ms \\ ns'}} E_{ms}^{(j)} g_{mnr}^{ss'} E_{ns'}^{(j)} \tag{2.13}$$

where index j numbers the excitation branches, and $E_{ms}^{(j)}$ are eigenvectors of the real part of the scattering matrix. They differ from eigenvectors of the general matrix (2.10) only by the value of the quantities A and B . For the nondegenerate eigenvalues, the eigenvectors of the real and imaginary parts of the scattering matrix coincide and (2.13) is exact. We note that equation (2.13) for the degenerate eigenvalue is correct because the degeneracy is connected with the symmetry properties of the matrix $g_{mnr}^{ss'}$, and the matrix $g_{mni}^{ss'}$ which has the same symmetry properties does not remove this degeneracy. Then, for the calculation of the higher-order terms, the degenerate eigenvalues are not considered.

Formula (2.13) is convenient because it allows one to separate the various processes which contribute to the X-ray absorption coefficient and to make a comparative estimation of these contributions. As is known, the normal absorption coefficient μ_0 is determined by inelastic processes of the following type: photoelectric dipole D , photoelectric quadrupole Q , thermal diffuse scattering (inelastic scattering by phonons) TDS and Compton scattering CS:

$$\mu_0 = \sum_P \mu_0^P, P = D, Q, \text{TDS, CS}.$$

The multiple-interference absorption coefficient, according to (2.13), can be also written as the sum of the contributions from the different processes:

$$\mu = \sum_P \mu^P = \sum_P \mu_0^P \left(\frac{\mu^P}{\mu_0^P} \right).$$

It should be noted that the ratio μ/μ_0 for the different inelastic processes can differ considerably.

The analysis of μ^D/μ_0^D is the most important because the dipole term of the photoelectric absorption is the overwhelming contribution to μ_0 . In this case the problem may be simplified essentially. Indeed, taking into consideration that the real and imaginary parts of the scattering matrix have in this case the same polarization dependence, we can replace the quantities χ_i^D by $\chi_i^D = \chi_i^D + i\chi_i^D$ in the formulae for $2\varepsilon_{0r}$ and then retain only the first two terms in the power series in i . The first term determines $2\varepsilon_{0r}$ and the second, divided by χ_{0i}^D , gives the necessary ratio.

In considering the symmetrical cases the dipole part of the Fourier components of the crystal polarizability depends only on the modulus of the reciprocal-lattice vector. Let us denote them by χ_m (without symbol D) in the order of increase of the modulus of the reciprocal-lattice vectors. The direct calculations give the following results. For $N=3$ (an equilateral triangle):

$$2\varepsilon_0^{(3)} = \left\{ \begin{array}{l} \chi_0 - \chi_1 + 3\chi_1 \sin^2 \theta \quad (3\pi) \\ \chi_0 - \chi_1 \quad (3\sigma) \\ \chi_0 + \frac{1}{2}\chi_1 [1 - 3Z_{\pm} \cos \theta] \\ \xi = \frac{\sin^2 \theta}{2 \cos \theta} \end{array} \right\} (1\pi, \sigma \pm). \tag{2.14}$$

For $N=4$ (a square):

$$2\varepsilon_0^{(4)} = \left\{ \begin{array}{l} \chi_0 - \chi_2 + 2[\chi_2 \pm \chi_1] \sin^2 \theta \quad (4\pi) \\ \chi_0 - \chi_2 \quad (2\pi) \\ \chi_0 + \chi_2 - 2\chi_1 Z_{\pm} \cos \theta \quad (4\sigma), (2\sigma) \\ \xi = \frac{\sin^2 \theta}{2 \cos \theta} \frac{\chi_2}{\chi_1} \end{array} \right\} (1\pi, \sigma \pm). \tag{2.15}$$

For $N=6$ (a regular hexagon):

$$2\varepsilon_0^{(6)} = \left\{ \begin{array}{l} \chi_0 \pm \chi_1 - \chi_2 \mp \chi_3 + \sin^2 \theta [\pm \chi_1 + 3\chi_2 \pm 2\chi_3] \\ \chi_0 \pm \chi_1 - \chi_2 \mp \chi_3 \\ \chi_0 - \chi_3 - \frac{1}{2}(\chi_1 - \chi_2)[1 + 3Z_{\pm} \cos \theta] \\ \xi = \frac{\sin^2 \theta}{6 \cos \theta} \frac{(\chi_1 + 3\chi_2 - 4\chi_3)}{(\chi_1 - \chi_2)} \\ \chi_0 + \chi_3 + \frac{1}{2}(\chi_1 + \chi_2)[1 - 3Z_{\pm} \cos \theta] \\ \xi = \frac{\sin^2 \theta}{6 \cos \theta} \frac{(4\chi_3 + 3\chi_2 - \chi_1)}{(\chi_1 + \chi_2)} \end{array} \right\} \begin{array}{l} (6\pi) \\ (3\pi) \\ (6\sigma) \\ (3\sigma) \\ (2\pi, \sigma \pm) \\ (1\pi, \sigma \pm) \end{array} \quad (2.16)$$

We note that (2.14)–(2.16) differ in the form of entry from the corresponding formulae in the paper of Joko & Fukuhara (1967). However, one can directly satisfy oneself that the formulae of Joko & Fukuhara (1967) for the eigenvalues of a dipole matrix can be identically transformed to the form (2.14)–(2.16) which is more convenient for analysis.

The complete field of X-rays in a crystal has the form

$$\mathbf{E}(\mathbf{r}) = \sum_j \lambda_j \exp(i\mathbf{k}_0^{(j)} \cdot \mathbf{r}) \sum_{ms} E_{ms}^{(j)} \mathbf{e}_{ms} \exp(i\mathbf{h}_m \cdot \mathbf{r}) \quad (2.17)$$

where λ_j is the excitement coefficient determined from the boundary conditions. The eigenvectors (2.11) are orthonormalized in the following way:

$$\sum_{ms} E_{ms}^{(j)} E_{ms}^{(j')} = \delta_{jj'}. \quad (2.18)$$

Taking this into account and assuming that the amplitude of the incident wave is equal to unity, one easily obtains

$$\lambda_j = \cos \varphi E_{0\pi}^{(j)} + \sin \varphi E_{0\sigma}^{(j)} \quad (2.19)$$

where φ is the angle between the polarization plane of the incident wave and the vector $\mathbf{e}_{0\pi}$. Therefore the π -polarized incident wave excited only ($n\pi$) solutions with the factor A , and the σ -polarized wave excites only ($n\sigma$) solutions with the factor B . In the limit of small scattering angles $\sin \theta \rightarrow 0$ and for the standard polarization only half the solutions are excited simultaneously in the crystal with the factor $1/\sqrt{N}$.

III. Analysis of the anomalous transmission effect

Let us consider, for the sake of simplicity, a crystal with atoms of the same type (e.g. germanium or silicon). In this case, as is seen from (2.3) and (2.5), the quantities χ_m are

$$\chi_{mr} = \chi_{0r} \frac{f_m}{Z} \exp(-W_m), \quad \chi_{mi}^D = \chi_{0i}^D \frac{Q}{Z} \exp(-W_m) \quad (3.1)$$

where f_m and $\exp(-W_m)$ are the form factor and the Debye–Waller factor for the scattering with the reciprocal-lattice vector \mathbf{h}_m , Z is the number of electrons.

The symmetrical three-wave case is considered by many authors (Joko & Fukuhara, 1967; Saccocio & Zajac, 1965; Penning, 1968; Kohn, 1975). In this case the formula (2.14) for nondegenerate solutions can be transformed into the form

$$\begin{array}{l} (1\pi, \sigma +): Z_+ = \frac{1}{\cos \theta}, \quad 2\varepsilon_0^{(3)} = \chi_0 - \chi_1 \\ (1\pi, \sigma -): Z_- = -\cos \theta, \quad 2\varepsilon_0^{(3)} = \chi_0 + 2\chi_1 - \frac{3}{2}\chi_1 \sin^2 \theta \end{array} \quad (3.2)$$

from which it follows that eigenvalues ($1\pi, \sigma +$) and (3σ) coincide accidentally. The minimum of the ratio μ^D/μ_0^D is determined just by these solutions and is

$$\mu_{\min}^{(3)} = \mu_0 [1 - \exp(-W_1)] \approx \mu_0 W_1 = \mu_0 B(T) h_1^2 \quad (3.3)$$

where $B(T) = 0.5 \langle u^2 \rangle$ is the factor which determines the temperature dependence and equals one half of the mean square displacement of atoms from their equilibrium positions. Consequently, in the three-wave case the dipole part of the photoabsorption is as in the two-wave case for σ -polarization and, roughly speaking, decreases by a factor W_1 .

Let us consider the four-wave case. As follows from (2.15), the eigenvalues (4σ) and (2σ) are accidentally degenerate. Their absorption coefficient is equal to that of the two-wave case, along the reciprocal-lattice vector \mathbf{h}_2 which corresponds to the diagonal of a square. The absorption coefficient for the (2π) solution is always less than for (2σ), and for (4π) it depends strongly on the parameter $\sin \theta = \lambda R/2\pi$ where λ is the wavelength of the radiation and R is the radius of the circumscribed circle of the reciprocal-lattice vector polygon. Among the degenerate solutions, ($1\pi, \sigma +$) is the most interesting one. Let us consider the limit of small scattering angles where $\sin \theta \ll 1$, i.e. $\lambda \ll a$, where a is the crystal lattice parameter. We express $2\varepsilon_0$ in the form of a power series in $\sin^2 \theta$ and take the imaginary part. Then we express the individual order terms as power series in W_1 and restrict ourselves to the first term in this series. Taking into consideration that \mathbf{h}_2 corresponds to the diagonal of a square and equation (3.3), we have the relation $W_2 = 2W_1$. As a result

$$\mu_{\min}^{(4)} \simeq \mu_0 \left[W_1^2 + W_1 \sin^2 \theta + \frac{1}{4} \left(1 - \frac{f_2}{f_1} \right) \sin^4 \theta + \dots \right]. \quad (3.4)$$

Thus, in the limit of small scattering angles the absorption coefficient decreases by a factor W_1^2 , and it is less essential than in the two-wave case. The new feature of this effect as compared with the two-wave case is the strong dependence on the scattering angle. If $\theta > \sqrt{W_1}$ then the second term in (3.4) becomes larger than the first and the effect grows gradually weak. We note that the absorption coefficient for the (2π) eigenvalue is near (4σ) and (2σ) in this case.

The other limiting case is a coplanar case where all the wave vectors lie in the plane of the reciprocal-lattice vectors and $\theta = \pi/2$. In this case μ for the $(1\pi, \sigma+)$ eigenvalue is near $(4\sigma, 2\sigma)$. The minimum absorption coefficient corresponds to the (2π) solution and is

$$\mu_{\min}^{(4)} \simeq \mu_0 [W_1^2 + 2W_1 \cos^2 \theta + \dots]. \quad (3.5)$$

Therefore in this limiting case one also has a decrease of μ by the factor W_1^2 in a narrow region of angles $\pi/2 > \theta > \pi/2 - \sqrt{0.5 W_1}$. We note that a very narrow interval of wavelengths corresponds to this region because $\sin \theta$ varies slightly for θ near $\pi/2$.

In a six-wave case there are three different values for the moduli of the reciprocal-lattice vectors, and $h_2^2 = 3h_1^2$, $h_3^2 = 4h_1^2$. Such relations exist for W quantities. The analysis of the nondegenerate roots is elementary. Expanding exponents in a power series in W_1 , we obtain.

$$\frac{\mu^{(6)}}{\mu_0} = \begin{cases} 6[W_1 + \sin^2 \theta + \dots] & (6\pi) \\ 3W_1^2 \cos^2 \theta + 2W_1^3 - 8W_1^3 \cos^2 \theta + \dots & (3\pi) \\ 6W_1 + \dots & (6\sigma) \\ 3W_1^2 + \dots & (3\sigma) \end{cases} \quad (3.6)$$

In the limit of small scattering angles the values of μ for π and σ solutions, as expected, coincide. It follows from (3.6) that the (3σ) eigenvalue results in the decrease of μ by a factor $3W_1^2$, i.e. a factor $3W_1$ less than in a two-wave case, independent of the scattering angle. However, the minimum value of μ corresponds to the (3π) solution for θ near to $\pi/2$. In this case μ decreases by a factor $2W_1^3$.

The $(2\pi, \sigma+)$ eigenvalue among the degenerate solutions is the most interesting one. In the small scattering angle limit, expanding as for the derivation of (3.4), we obtain

$$\mu_{\min}^{(6)} \simeq \mu_0 [2W_1^3 + \frac{3}{2}W_1^2 \sin^2 \theta + \dots]. \quad (3.7)$$

Hence, for small scattering angles the absorption coefficient decreases as compared with μ_0 as strongly as in the coplanar case, but for a different type of electromagnetic field. We note that there is here a very strong suppression of the dipole part of a photoabsorption. So for a Ge crystal and the 220 reflexion

the quantity W_1 is 0.0356 for $T = 300$ K. Therefore, in this case a decrease of μ by a factor $2W_1^3 = 0.905 \times 10^{-4}$ is equivalent to an increase of the crystal thickness accessible to X-rays, by approximately 10^4 times. However, the complete analysis of the Borrmann effect needs a calculation of the other absorption mechanisms, in particular, quadrupole absorption.

Before passing on to the analysis of the quadrupole part of photoabsorption, we make clear the physical mechanism of the suppression of a dipole interaction. As is known, in the two-wave case the decrease of absorption arises as a result of the formation in the crystal of a standing wave, the nodes of which just coincide with the sites of a crystal lattice. In the dipole case the atoms are approximated by point dipoles.

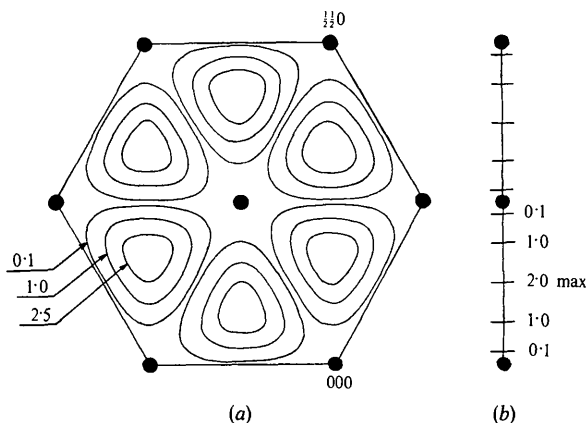


Fig. 1. The X-ray energy density between the atoms of a crystal in the six-wave case for Ag $K\alpha$ -radiation and $(2\pi, \sigma+)$ eigenvector.

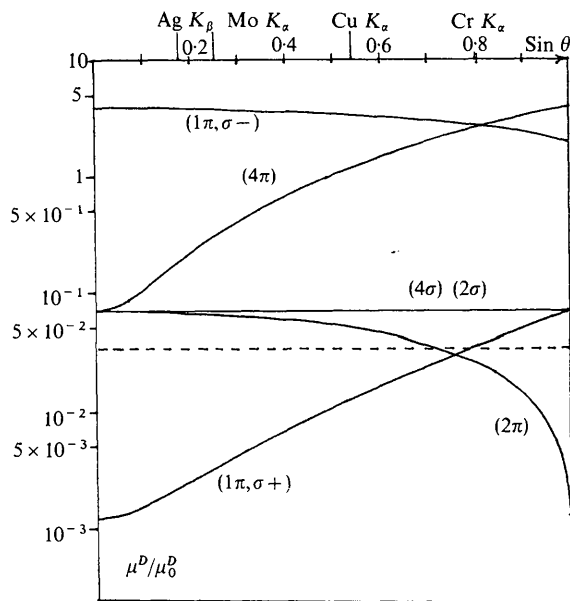


Fig. 2. The ratio μ/μ_0 for the D process for the four-wave case in germanium (on a logarithmic scale).

The absorption would disappear if the thermal vibrations were absent. Actually, owing to thermal vibrations, the interaction between the electrons of the

atoms and the electric field nevertheless occurs, but with less intensity than for a plane wave where the energy density distributes uniformly over all the crystal. Expanding the space dependence of the field at the lattice sites in a Taylor series and considering that the first derivatives do not equal zero, one easily obtains after averaging over the thermal vibrations that $\mu \sim \langle u^2 \rangle \sim W$ in this case.

A different character of interaction between the electrons of the atoms and the field arises when the first derivatives of the field amplitude are equal to zero at the lattice sites. In this case the Taylor expansion at a site begins with u^2 , and $\mu \sim \langle u^4 \rangle \sim W^2$. This type of electric-field structure arises in several excitation modes of four-wave and six-wave cases. It can be directly verified with the formulae (2.11), (2.15), (2.16). Analogously, when $\mu \sim W^3$, the tensor of the second derivatives of the field amplitude is also equal to zero at the crystal lattice site.

Fig. 1 shows the lines of equal energy density between the atoms, divided by the value integrated over all the unit cell, for a regular hexagon with a (220) face in germanium. The calculation was done for Ag $K\alpha$ radiation ($\lambda = 0.559 \text{ \AA}$), $T = 300 \text{ K}$ and a $(2\pi, \sigma +)$ eigenvector. As seen from the figure, the space dependence of the field is characterized by the point symmetry of the lattice in the $(1\bar{1}1)$ plane with narrow and high maxima just between the atoms and rather wide regions of weak field near the lattice sites. The radius of the black circles is $\sqrt{\langle u^2 \rangle}$. Fig. 1(b) shows, for the sake of comparison, the space dependence (along the $[110]$ direction) for the 220, two-wave case and σ polarization. We note that the form of the minimum, narrow valleys connecting the atoms of the triangular lattice, is typical for the degenerate solutions and wavelengths which correspond to weak absorption. For nondegenerate solutions (3σ) , (3π) the lines have a different character, *i.e.* close hexagons enveloping the minimum region [see the figure in Huang, Tillinger & Post (1973)].

The calculation of the ratio μ/μ_0 for quadrupole photoabsorption can be done with (2.13). One also easily obtains the analytical expressions connecting the ratio μ/μ_0 with the quantities χ_m , ξ and $\sin \theta$. However, for the degenerate solutions these formulae are very cumbersome and we do not give them here. We note only two circumstances.

The first is that in the limit $\sin \theta = 0$ all the vectors \mathbf{s}_m are equal to one another, *i.e.* $(\mathbf{s}_m \mathbf{s}_n) = 1$, and \mathbf{e}_{ms} is perpendicular to \mathbf{s}_n . Then, as seen from (2.10), the quadrupole polarization matrix coincides with a dipole matrix and also the ratios μ/μ_0 for the D and Q processes coincide. Thus, in this region of angles suppression of the quadrupole photoabsorption takes place as strongly as the dipole suppression. It may be noticed that this conclusion is correct also for higher-order multipoles.

The second circumstance is that in accordance with (2.10) and (2.13) the ratio μ^Q/μ_0^Q is proportional to the

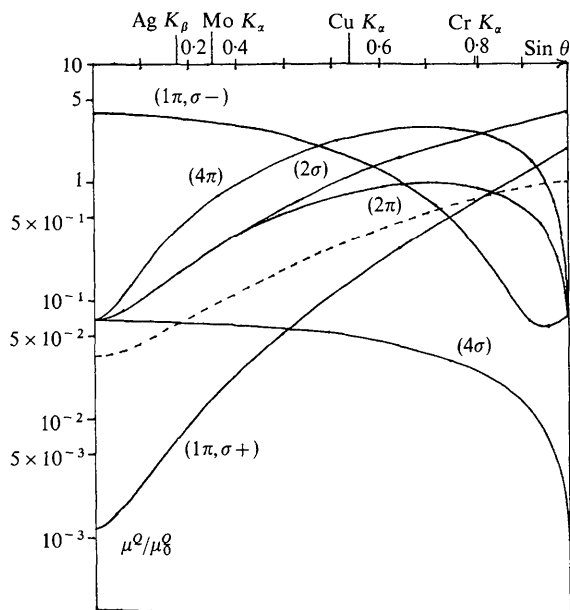


Fig. 3. The ratio μ/μ_0 for the Q process for the four-wave case in germanium (on a logarithmic scale).

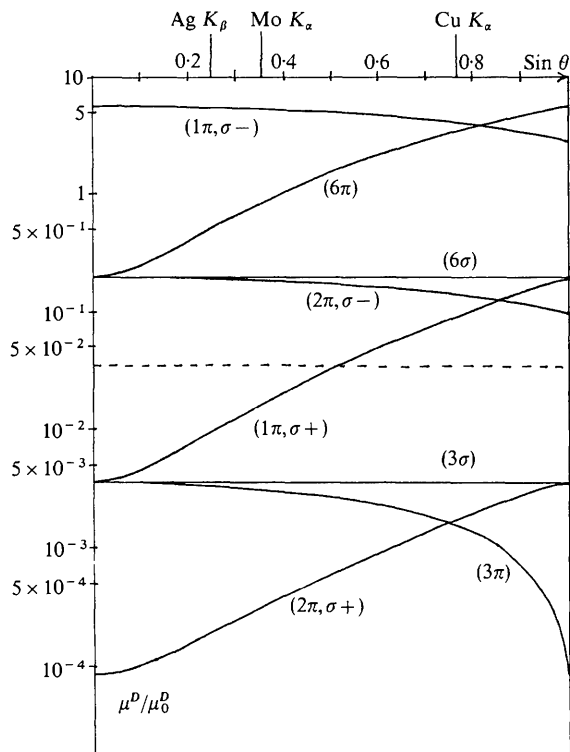


Fig. 4. The ratio μ/μ_0 for the D process for the six-wave case in germanium (on a logarithmic scale).

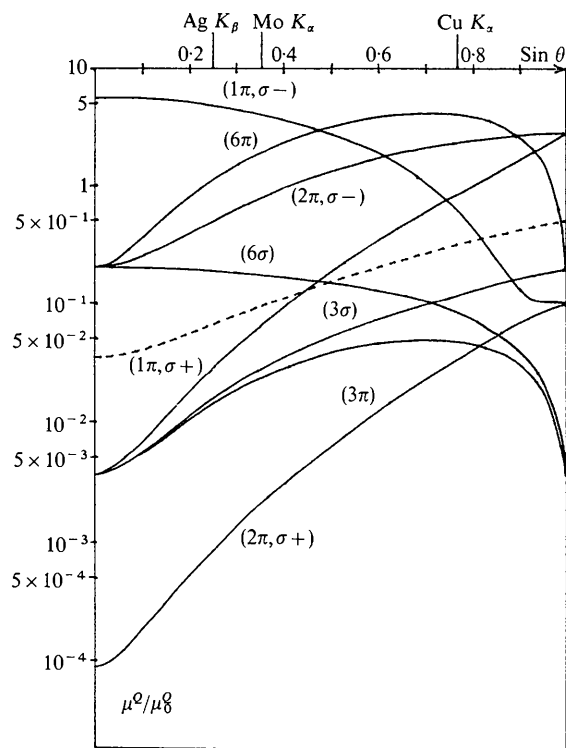


Fig. 5. The ratio μ/μ_0 for the Q process for the six-wave case in germanium (on a logarithmic scale).

product $s_n^i E_m^k$, where i, k are the vector indices. In real space these products correspond to the first derivatives of the field amplitude. Expanding the space dependence of the field energy density at a lattice site in the general case, one easily concludes that the first term of the expression for μ^Q/μ_0^Q as a power series in W has an index less by one than for the dipole interaction, analogous to the two-wave case. Because the ratio σ^Q/σ^D for X-rays is less, precisely speaking, than W_1 , the calculation of μ^Q does not indicate disorder of the Borrmann effect of any power.

Figs. 2–5 show the calculated dependence of the ratio μ/μ_0 on $\sin \theta$ for D and Q processes (on a logarithmic scale) for the four-wave and six-wave cases with the (220) face in germanium and $T = 300$ K. The constant B in this case is 0.00362 \AA^2 [$T_D = 290^\circ \text{K}$ according to Batterman & Chipman (1962)]. The form-factor values used are taken from Doyle & Turner (1968). The values of $\sin \theta$ corresponding to the wave lengths of the most spread sources are shown also along the abscissa. As seen from the figures, $\text{Cu } K\alpha$ radiation, which was used by Joko & Fukuhara (1967), Huang, Tillinger & Post, (1973) and Kshevetskii & Myhailuk (1976), is the most unsuitable. A stronger effect is obtained for hard radiation with a small wavelength. The dotted lines correspond to the two-wave case for σ polarization.

The absolute value of the absorption coefficient with account taken of the photoelectric mechanism only can be calculated by

$$\mu = \mu_0^{\text{exp}} \frac{\sigma^D}{(\sigma^D + \sigma^Q)} \left[\left(\frac{\mu}{\mu_0} \right)^D + \frac{\sigma^Q}{\sigma^D} \left(\frac{\mu}{\mu_0} \right)^Q \right]. \quad (3.8)$$

Table 1 shows the calculated values of the minimum and following absorption coefficients in the six-wave case. The data for the calculation are taken from Hildebrandt, Stephenson & Wagenfeld (1973).

Table 1. The minimum absorption coefficients

λ (Å)	μ^D/μ_0^D	μ^Q/μ_0^Q	σ^Q/σ^D	μ_0^{exp} (cm^{-1})	μ (cm^{-1})	$\mu_{220}^{(2)}$ (cm^{-1})
0.559	2.31×10^{-4}	1.16×10^{-3}	0.0406	169	0.045	5.94
0.709	3.29×10^{-3}	1.71×10^{-2}	0.026	320	0.645	11.5
1.54	3.28×10^{-4}	2.19×10^{-3}	0.0234	354	0.120	14.4
	3.13×10^{-3}	2.40×10^{-2}			0.976	
	1.77×10^{-3}	3.53×10^{-2}			0.898	
	1.51×10^{-3}	4.80×10^{-2}			0.909	

It should be noted that the data of Table 1 are of preliminary character. Indeed, under the condition of photoabsorption being so strongly suppressed, the TDS and CS processes may play an appreciable part. The analysis of the ratio μ/μ_0 for these processes is a rather complicated problem. It will be considered in a separate paper. We note here only that although suppression of these inelastic processes will take place it will be not as strong as for the photoeffect. Indeed, all the electrons of an atom take part in these processes, in particular the valence electrons. Since the density of valence electrons spreads practically over all the crystal, no reconstruction of the wave function of the field can suppress the processes they take part in.

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