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Normal and Anomalous Photoelectric Absorption of X Rays in Crystals

H. Wagenfeld*
School of Physics, University of Melbourne, Parkville, Victoria, Australia

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The photoelectric absorption of x rays in atoms (K-, L-, and M-shell) is discussed for the nonrelativistic region, taking retardation effects into account. This is done by expanding the retardation factors in the transition probabilities in a Taylor series and this corresponds to an expansion in terms of electric multipoles. This expansion converges very rapidly and even the octupole transitions may be neglected. In the case of the anomalous absorption of x rays in perfect single crystals (Borrmann effect), the absorption cross sections become angular-dependent. This angular dependence allows in principle a direct experimental determination of the quadrupole term of the atomic photoelectric absorption cross section. Measurements by several authors indicate the existence of the electric quadrupole transitions.

INTRODUCTION

THE effect of anomalous transmission of x rays occurs in perfect single crystals if the vacuum wave fulfills a Laue condition for one reflecting lattice plane inside the crystal (Borrmann effect).[1] The effect itself has been discussed by several authors and more detailed information can be found in Batterman's and Cole's recent review article[2] about this subject. The present paper deals rather with the absorption processes itself. The formal connection between the photoelectric absorption coefficient and the corresponding quantity in the case of the Borrmann effect was previously pointed out by the author.[3] The formula given there can be regarded as a special case of a formula derived earlier by Molière.[4] Molière neglected the influence of the thermal vibrations inside the crystal. Recently, Ohtsuki[5] has shown that the temperature dependence has to be derived by a Debye-Waller factor. This result agrees with assumptions made by Batterman[6] and the author.[3] Comparative measurements of the anomalous transmission at room temperature and higher temperatures by Batterman[7] and Okkerse,[8] at room temperature only by Hildebrandt,[9] and at room temperature and liquid nitrogen temperature by Ling and the author,[10] confirm this result.

Apart from the Debye-Waller factor the absorption coefficient shows, in the case of the Borrmann effect, an angular dependence which for a special polarization direction of the x rays is caused by electrical quadrupole transititions of the photoelectrons only. In spite of the very low probability for such processes relative to the dipole transitions, recent measurements by Hildebrandt[9] indicate clearly the existence of the transitions.

In the first part of the paper we give a review of results for the normal photoelectric effect. All the results mentioned here are based on the nonrelativistic approximation, and the wave functions are hydrogen-like eigenfunctions. The retardation factors in the transition probabilities are expanded in a Taylor series which corresponds to an expansion in electrical multipoles. In the second part of this paper we discuss the connection with the Borrmann effect and propose a method by which it should be possible to determine separately the dipole and quadrupole term of the atomic absorption cross section and the Debye-Waller factor as well.

A. NORMAL PHOTOELECTRIC ABSORPTION IN ATOMS

The atomic photoelectric absorption cross section is defined by the equation[11]:

$$\sigma_A=(4\pi^2e^2\hbar^2/m^2c^2K)\left|\textstyle\sum_i\langle W|\nabla_i\mathbf{E}_0e^{i\mathbf{K}\cdot\mathbf{r}_i}|G\rangle\right|^2,\quad(1)$$

where $\mathbf{E}_0$ is the polarization direction of the x rays (unit vector), $\mathbf{K}$ is the wave vector of the x rays ($K=2\pi/\lambda$), $\hbar$ is Planck's constant divided by 2π, c is the velocity of light, e is the electron charge and $\mathbf{r}_i$ is the position vector of the ith atomic electron. The sum in (1) is to be extended over all atomic electrons. $|G\rangle$ is a wave function for the ground state and $|W\rangle$ is the corresponding wave function of an excited state, i.e., a state in which one or more electrons are free (bound-free transitions). In order to simplify the calculations we replace the atomic wave functions by hydrogen-like eigenfunctions (i.e., one-electron wave functions corrected for inner screening) and obtain:

$$\sigma_A=\frac{8\pi^2e^2\hbar^2}{m^2c^2K}\sum_{l',m'}\sum_{n,l,m}\left|\langle\rho'|\frac{\partial}{\partial y}e^{iKx}|\rho\rangle\right|^2.\quad(2)$$

Here we have assumed that the propagation direction of the x rays is the x axis and the polarization direction is the y axis of a Cartesian coordinate system. $\rho=n,\ l,\ m$

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are the quantum numbers of a bound electron and $\rho'=n', l', m'$ are the quantum numbers of the ejected free electron $[n'=(Z-s)/ia_0k$, Z is the atomic number, s is Slater's screening constant, k is the wave vector of the emitted electron, and $a_0=\hbar^2/me^2$ is the first Bohr radius$]$. For the usual representation of the hydrogen eigenfunctions for the discrete and the continuum state compare, e.g., Ref. 11 or 12.

In order to determine the angular distribution of the ejected photoelectrons, special consideration must be made of retardation effects. The photoelectric effect has been discussed for the K and L shell by Sauter,[13] using polar coordinates, and by Fischer,[14] using parabolic coordinates. Fischer publishes as well a formula for the x-ray absorption cross section of the two K electrons taking retardation effects fully into account. If one neglects terms of the order $\hbar\omega/2mc^2$, v^2/c^2 relative to unity ($v=k\hbar/m$, the velocity of the emitted free electron), then Fischer's formula is identical with a formula derived earlier by Nishina and Rabi[15] for the dipole approximation. One obtains the dipole approximation by choosing the retardation factor in (1) or (2), respectively equal to one. In this approximation, Fischer[14] published a formula for the absorption cross section including the s and p electrons of the L shell. The formulas separated for the s and p electrons are published by Stobbe.[16] Even before Fischer's and Sauter's publications, Schur and Sommerfeld[17] did calculations in connection with the forward intensity shift of the photoelectrons relative to the polarization direction of the x rays by expanding the retardation factor in a Taylor series

$$\exp(iKx)=1+iKx-\tfrac{1}{2}K^2x^2-\cdots.$$

This treatment corresponds to a multipole expansion. They considered only the term $(1+iKx)$ which corresponds, since

$$\langle\rho'|(1+iKx)\frac{\partial}{\partial y}|\rho\rangle=\frac{m\omega}{\hbar}\langle\rho'|y|\rho\rangle-\frac{im\omega^2}{2c\hbar}\langle\rho'|xy|\rho\rangle,$$

to electrical dipole and quadrupole transitions.[18] Schur and Sommerfeld did not publish absorption cross sections. Since there is, particularly in connection with the Borrmann effect, a strong interest in obtaining accurate values for the absorption cross sections, we calculated the quadrupole and octupole terms for the K and L shell as well. The absorption cross section for all 18 electrons of the M shell using the dipole approximation has been published by Hall.[19] Since we are interested in the contributions of the different subshells, we recalculated these absorption cross sections and found Hall's formula not in agreement with our result. For short wavelength the formula is generally too large by a factor of 3. On the other hand Harriman[20] calculated Bethe's "average excitation potentials" for the states 1s through 4s of hydrogen. These results are related to our calculations, and we found complete agreement for the M electrons. Hönl[21] and Eisenlohr and Müller[22] did calculations in connection with the atomic dispersion theory for x rays by evaluating the generalized atomic scattering factor derived by Waller, for the K and L shell. Some of their results are in close relation to some of the formulas given here. We have been interested in the convergence of the multipole expansion, particularly for the case in which the wavelength of the radiation is small in comparison with the absorbing electron shell radius. Therefore we calculated the octupole terms for the 1s, 2s, and 2p electrons as well. The procedures for calculating matrix elements of the form (2) are standard methods and therefore need not be discussed here (cf. e.g. Refs. 11, 12). The absorption cross sections are given separately for the dipole, quadrupole and octupole terms of the different electron shells. We denote the angular momentum quantum number for the initial state by l and for the final state by l'. The selection rules are

$$\begin{array}{ll} \text{dipole} & l\rightarrow l'=l\pm1, \\ \text{quadrupole} & l\rightarrow l'=l\pm2,\ l'=l, \\ \text{octupole} & l\rightarrow l'=l\pm1,\ l\pm3, \\ & \qquad (\text{for } l=0,\ l'=l \text{ forbidden}). \end{array}$$

The different absorption cross sections for the dipole, quadrupole, and octupole transitions are denoted by the suffixes D, Q, and O, respectively. For example $\sigma_{1s}{}^{Q}$ means the quadrupole absorption cross section of an electron in the K shell.

Absorption Cross Sections for the *K* Shell

Since $l=0$ for the two K-shell electrons, we have the transitions $l'=1$ for the dipole, $l'=2$ for the quadrupole, and $l'=1$ or 3 for the octupole terms. There is, further, a mixed term for $l'=1$ (dipole-octupole term) which has

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the same magnitude as the quadrupole term.[23] We obtain[24]

$$\sigma_{1s}{}^{D}=\frac{2^{7}}{3}\pi r_{0}\lambda\left(\frac{\lambda}{\lambda_{1}}\right)^{3}\frac{\exp(-4n_{1}'\cot^{-1}n_{1}')}{1-\exp(-2\pi n')}, \tag{3a}$$

$$\sigma_{1s}{}^{Q}=\tfrac{2}{5}\sigma_{1s}{}^{D}\cdot(\lambda_{c}/\lambda)(4-3\lambda/\lambda_{1}), \tag{3b}$$

$$\begin{aligned}\sigma_{1s}{}^{O}&=\frac{1}{350}\sigma_{1s}{}^{D}\left(\frac{\lambda_{c}}{\lambda}\right)^{2}\left(59-366\frac{\lambda}{\lambda_{1}}+296\left(\frac{\lambda}{\lambda_{1}}\right)^{2}\right),\quad l'=1,\\ &=\frac{8}{175}\sigma_{1s}{}^{D}\left(\frac{\lambda_{c}}{\lambda}\right)^{2}\left(4-3\frac{\lambda}{\lambda_{1}}\right)\left(9-8\frac{\lambda}{\lambda_{1}}\right),\quad l'=3,\end{aligned} \tag{3c}$$

$$\sigma_{1s}{}^{D,O}=\tfrac{2}{5}\sigma_{1s}{}^{D}(\lambda_{c}/\lambda)(1-2\lambda/\lambda_{1}), \tag{3d}$$

for the absorption cross section per electron. Here λ_1 is the wavelength which corresponds to the hydrogen-like energy eigenvalue of the 1s-state:

$$\lambda_{1}=[(Z-s_{1})^{2}R_{\infty}]^{-1},\quad n_{1}'=[\lambda/(\lambda_{1}-\lambda)]^{1/2}. \tag{4}$$

$R_{\infty}=2\pi^{2}me^{4}/h^{3}c=109737.3\text{ cm}^{-1}$ Rydgerg constant,
$r_{0}=e^{2}/mc^{2}=2.8179\cdot10^{-13}\text{ cm}$,
$\lambda_{c}=h/mc=24.263\cdot10^{-11}\text{ cm}$ Compton wavelength,
$s_{1}=0.30$ Slater's screening constant for the K shell,
$Z=$ atomic number,
$\lambda=$ x-ray wavelength.

Within the nonrelativistic region (i.e., $\lambda_{c}\ll\lambda$, $Z^{2}\alpha^{2}\ll1$, where α is Sommerfeld's fine structure constant, $\alpha=e^{2}/\hbar c=1/137.04$) the multipole expansion converges very rapidly. For $\lambda\ll\lambda_{1}$, we obtain from the formulas above[25]

$$\frac{\sigma_{1s}{}^{Q}}{\sigma_{1s}{}^{D}}=1.60\frac{\lambda_{c}}{\lambda};\quad\frac{\sigma_{1s}{}^{O}}{\sigma_{1s}{}^{D}}\simeq1.65\left(\frac{\lambda_{c}}{\lambda}\right)^{2}\simeq\frac{\lambda_{c}}{\lambda}\frac{\sigma_{1s}{}^{Q}}{\sigma_{1s}{}^{D}}. \tag{5}$$

In (5) we considered only $\sigma_{1s}{}^{O}$ for $l'=3$, since $\sigma_{1s}{}^{O}(l'=1)<\sigma_{1s}{}^{O}(l'=3)$. The total absorption cross section for the two electrons of the K shell is given by

$$\begin{aligned}\sigma_{1s}&=2[\sigma_{1s}{}^{D}+\sigma_{1s}{}^{Q}+\sigma_{1s}{}^{O}(l'=1)+\sigma_{1s}{}^{O}(l'=3)+\sigma_{1s}{}^{D,O}]\\ &=\frac{2^{8}\pi r_{0}}{3}\frac{\lambda^{4}}{\lambda_{1}{}^{3}}\left[1+2\frac{\lambda}{\lambda_{c}}\left(1-\frac{\lambda}{\lambda_{1}}\right)+\frac{1}{350}\left(\frac{\lambda_{c}}{\lambda}\right)^{2}\left(635-1310\frac{\lambda}{\lambda_{1}}+680\left(\frac{\lambda}{\lambda_{1}}\right)^{2}\right)\right]\frac{\exp(-4n_{1}'\cot^{-1}n_{1}')}{1-\exp(-2\pi n_{1}')}.\end{aligned} \tag{6}$$

Absorption Cross Section of the L Shell

The absorption cross section of the L shell may be determined by[26]

$$\sigma_{2s}{}^{D}=\frac{2^{10}}{3}\pi r_{0}\lambda\left(\frac{\lambda}{\lambda_{2}}\right)^{3}\left(1+3\frac{\lambda}{\lambda_{2}}\right)\frac{\exp(-4n_{2}'\cot^{-1}\tfrac{1}{2}n_{2}')}{1-\exp(-2\pi n_{2}')}, \tag{7a}$$

$$\sigma_{2s}{}^{Q}=\frac{8}{5}\sigma_{2s}{}^{D}\frac{\lambda_{c}}{\lambda}\left(\frac{\lambda}{\lambda_{2}}-1\right)^{2}, \tag{7b}$$

$$\begin{aligned}\sigma_{2s}{}^{O}&=\frac{32}{175}\sigma_{2s}{}^{D}\left(\frac{\lambda_{c}}{\lambda}\right)^{2}\left(1-2\frac{\lambda}{\lambda_{2}}\right)\left(9-5\frac{\lambda}{\lambda_{2}}\right),\quad(l'=3)\\ &=\frac{1}{350}\sigma_{2s}{}^{D}\left(\frac{\lambda_{c}}{\lambda}\right)^{2}\left(59-436\frac{\lambda}{\lambda_{2}}+296\left(\frac{\lambda}{\lambda_{2}}\right)^{2}\right),\quad(l'=1),\end{aligned} \tag{7c}$$

$$\sigma_{2s}{}^{D,O}=\tfrac{2}{5}\sigma_{2s}{}^{D}(\lambda_{c}/\lambda)(1-2\lambda/\lambda_{2}), \tag{7d}$$

$$\lambda_{2}=4/(Z-s_{2})^{2}R_{\infty};\quad n_{2}'=2[\lambda/(\lambda_{2}-\lambda)]^{1/2}. \tag{8}$$

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[23] That there exists a dipole-octupole term, can be seen from the relation:

$$\langle\rho'|(1+iKx-\tfrac{1}{2}K^{2}x^{2})\frac{\partial}{\partial y}|\rho\rangle\langle\rho|(1-iKx-\tfrac{1}{2}K^{2}x^{2})\frac{\partial}{\partial y}|\rho'\rangle=\langle\rho'|\frac{\partial}{\partial y}|\rho\rangle^{2}+K^{2}\langle\rho'|\frac{\partial}{\partial y}x|\rho\rangle^{2}+\frac{K^{4}}{4}\langle\rho'|\frac{\partial}{\partial y}x^{2}|\rho\rangle^{2}-K^{2}|\langle\rho'|x^{2}\frac{\partial}{\partial y}|\rho\rangle\langle\rho|\frac{\partial}{\partial y}|\rho'\rangle|.$$

[24] The formula (3a) was first published by Nishina and Rabi (Ref. 15). The formulas (3b) and (3d) are related to the quantities $f_{1}{}^{(2)}$ and $f_{2}{}^{(2)}$ in the paper by Hönl (Ref. 21).

[25] The opinion often found in some books and publications (e.g., Refs. 12 and 22), that the multipole expansion does converge if the ratio of the electron-shell extension to the x-ray wavelength is small, seems to be irrelevant, since the convergence is independent of this ratio.

[26] The formulas (7a) and (11a) were first published by M. Stobbe (Ref. 15), and the Eqs. (7b), (7d), (11b), and (11d) are related to the quantities $f_{1}{}^{s(2)}$, $f_{2}{}^{s(2)}$, $f_{1}{}^{P(2)}$, $f_{2}{}^{P(2)}$, respectively, in the paper by Eisenlohr and Müller (Ref. 22). The term $f_{2}{}^{s(2)}$ has to be $f_{2}{}^{s(2)}=(2^{11}/15)[(z-1)(z+3)/z^{7}]g(Z)$.

For $\lambda \ll \lambda_2$ we obtain the same relation as in Eq. (5):

$$\frac{\sigma_{2s}{}^{Q}}{\sigma_{2s}{}^{D}}=1.60\frac{\lambda_c}{\lambda},\quad \frac{\sigma_{2s}{}^{O}}{\sigma_{2s}{}^{D}}=1.65\left(\frac{\lambda_c}{\lambda}\right)^2\simeq\frac{\lambda_c}{\lambda}\frac{\sigma_{2s}{}^{Q}}{\sigma_{2s}{}^{D}}. \tag{9}$$

The total absorption cross section for the two $2s$ electrons, neglecting terms which are quadratic in λ_c/λ, is given by

$$\begin{aligned}\sigma_{2s}&=2[\sigma_{2s}{}^{D}+\sigma_{2s}{}^{Q}+\sigma_{2s}{}^{D,O}]\\ &=\frac{2^{11}}{3}\pi r_0\lambda\left(\frac{\lambda}{\lambda_2}\right)^2\left(1+3\frac{\lambda}{\lambda_2}\right)\left\{1+2\frac{\lambda}{\lambda_c}\left[1-2\frac{\lambda}{\lambda_2}+\frac{4}{5}\left(\frac{\lambda}{\lambda_2}\right)^2\right]\right\}\frac{\exp(-4n_2'\cot^{-1}\frac{1}{2}n_2')}{1-\exp(-2\pi n_2')}.\end{aligned} \tag{10}$$

We obtain for the $2p$ electrons

$$\sigma_{2p}{}^{D}=\frac{2^{10}}{3}\pi r_0\lambda\left(\frac{\lambda}{\lambda_2}\right)^4\left(1+\frac{8}{3}\frac{\lambda}{\lambda_2}\right)\frac{\exp(-4n_2'\cot^{-1}\frac{1}{2}n_2')}{1-\exp(-2\pi n_2')}, \tag{11a}$$

$$\sigma_{2p}{}^{Q}=\tfrac{4}{5}\sigma_{2p}{}^{D}\frac{\lambda_c}{\lambda}\frac{(11-6\lambda/\lambda_2)(1+3\lambda/\lambda_2)}{(3+8\lambda/\lambda_2)}, \tag{11b}$$

$$\sigma_{2p}{}^{D,O}=\tfrac{2}{5}\sigma_{2p}{}^{D}(\lambda_c/\lambda)(1-2\lambda/\lambda_2). \tag{11c}$$

Here we mention the results only up to the dipole-octupole term. The previous results showed that the octupole terms are very small in comparison with the dipole terms and therefore can be neglected within the limits of the theory in any sort of practical calculations.[27] If for $\lambda \ll \lambda_2$, the octupole terms for the $2s$ electrons are small, then this approximation is even more valid for the term $\sigma_{2p}{}^{O}$, since

$$\sigma_{2p}{}^{O}\sim(\lambda/\lambda_2)\sigma_{2s}{}^{O}. \tag{12}$$

We obtain for $\lambda \ll \lambda_2$

$$\sigma_{2p}{}^{Q}/\sigma_{2p}{}^{D}\simeq 2.93\lambda_c/\lambda. \tag{13}$$

The total absorption cross section for the six $2p$ electrons is

$$\begin{aligned}\sigma_{2p}&=6[\sigma_{2p}{}^{D}+\sigma_{2p}{}^{Q}+\sigma_{2p}{}^{D,O}]\\ &=\frac{2^{11}}{3}\pi r_0\lambda\left(\frac{\lambda}{\lambda_2}\right)^4\left\{3+8\frac{\lambda}{\lambda_2}+\frac{2}{5}\frac{\lambda}{\lambda_c}\left(25+56\frac{\lambda}{\lambda_2}-52\left(\frac{\lambda}{\lambda_2}\right)^2\right)\right\}\frac{\exp(-4n_2'\cot^{-1}\frac{1}{2}n_2')}{1-\exp(-2\pi n_2')}.\end{aligned} \tag{14}$$

Absorption Cross Sections for the *M* Shell

The absorption cross sections for the M shell may be determined by[28]

$$\sigma_{3s}{}^{D}=2^7\pi r_0\lambda\left(\frac{\lambda}{\lambda_3}\right)^3\left(9+96\frac{\lambda}{\lambda_3}+208\left(\frac{\lambda}{\lambda_3}\right)^2+128\left(\frac{\lambda}{\lambda_3}\right)^3\right)\times\frac{\exp(-4n_3'\operatorname{cot}n^{-1}\frac{1}{3}n_3')}{1-\exp(-2\pi n_3')}, \tag{15a}$$

$$\sigma_{3s}{}^{Q}=\tfrac{2}{5}\sigma_{3s}{}^{D}\frac{\lambda_c}{\lambda}\left(4+5\frac{\lambda}{\lambda_3}\right)\frac{(3-4\lambda/\lambda_3)}{3+4\lambda/\lambda_3}, \tag{15b}$$

$$\sigma_{3s}{}^{D,O}=\tfrac{4}{5}\sigma_{3s}{}^{D}\frac{\lambda_c}{\lambda}\left(1-2\frac{\lambda}{\lambda_3}\right)\frac{(3+4\lambda/\lambda_3)}{3-2\lambda/\lambda_3}, \tag{15c}$$

with

$$\lambda_3=9/(Z-s_3)^2R_\infty \quad\text{and}\quad n_3'=3[\lambda/(\lambda_3-\lambda)]^{1/2}. \tag{16}$$

For $\lambda \ll \lambda_3$ it follows

$$\sigma_{3s}{}^{Q}/\sigma_{3s}{}^{D}\simeq 1.60\lambda/\lambda_c. \tag{17}$$

This result corresponds to (5) and (9). Since we have used hydrogen-like eigenfunctions throughout, we may expect that the formulas for the absorption cross sections of the M electrons hold for $\lambda < \lambda_2$ only, i.e., we can consider these equations only as the M-shell contributions to the K- and L-shell absorption. In this region $\lambda \ll \lambda_3$ is certainly fulfilled and according to Eq. (17) the contribution of the quadrupole term is negligible.

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[27] We calculated the octupole terms for the $2p$ electrons as well and the results confirm the argument given above. The latter calculations were carried out with the assistance of Dr. A. L. Chaudhuri (University of Dacca, Pakistan). The author would like to thank him very much for his help and several stimulating discussions.

[28] The formulas for the dipole absorption cross sections are directly related to results by Harriman (Ref. 20) in connection with "Bethe's excitation potentials."

Because

$$\sigma_{3p}{}^{Q} \sim (\lambda/\lambda_3)\sigma_{3s}{}^{Q} \quad \text{and} \quad \sigma_{3d}{}^{Q} \sim (\lambda/\lambda_3)^2 \sigma_{3s}{}^{Q} \tag{18}$$

this holds more closely for the quadrupole terms of the *p*- and *d*-electrons of this shell. We therefore do not consider these terms further and mention only the dipole terms:

$$\sigma_{3p}{}^{D} = 2^{10}\pi r_0 \lambda \left(\frac{\lambda}{\lambda_3}\right)^4 \left[3 + 26\frac{\lambda}{\lambda_3} + 28\left(\frac{\lambda}{\lambda_3}\right)^2\right] \times \frac{\exp(-4n_3' \cot^{-1}\frac{1}{3}n_3')}{1-\exp(-2\pi n_3')}, \tag{19}$$

$$\sigma_{3d}{}^{D} = \frac{2^{11}}{5}\pi r_0 \lambda \left(\frac{\lambda}{\lambda_3}\right)^5 \left[5 + 46\frac{\lambda}{\lambda_3} + 48\left(\frac{\lambda}{\lambda_3}\right)^2\right] \times \frac{\exp(-4n_3' \cot^{-1}\frac{1}{3}n_3')}{1-\exp(-2\pi n_3')}. \tag{20}$$

The total absorption cross section for the 18 electrons of the *M* shell is given by

$$\sigma_M = 2\sigma_{3s}{}^{D} + 6\sigma_{3p}{}^{D} + 10\sigma_{3d}{}^{D}. \tag{21}$$

Since the screening constant for a 3*d* electron differs considerably from the screening constant of a 3*s* or 3*p* electron, it is not useful to define a closed expression for the total absorption cross section of the *M* shell.

Absorption Cross Sections for the 4*s* and 4*p* Electrons

The absorption cross sections for the 4*s* and 4*p* electrons may be determined by[29]

$$\sigma_{4s}{}^{D} = \frac{2^{13}}{9}\pi r_0 \lambda \left(\frac{\lambda}{\lambda_4}\right)^3 \left[3 + 69\frac{\lambda}{\lambda_4} + 424\left(\frac{\lambda}{\lambda_4}\right)^2 + 1024\left(\frac{\lambda}{\lambda_4}\right)^3 + \frac{2944}{3}\left(\frac{\lambda}{\lambda_4}\right)^4 + 320\left(\frac{\lambda}{\lambda_4}\right)^5\right] g(n_4'), \tag{22}$$

$$\sigma_{4p}{}^{D} = \frac{2^{13}}{15}\pi r_0 \lambda \left(\frac{\lambda}{\lambda_4}\right)^4 \left[75 + 1400\frac{\lambda}{\lambda_4} + 5304\left(\frac{\lambda}{\lambda_4}\right)^2 + 6016\left(\frac{\lambda}{\lambda_4}\right)^3 + 2112\left(\frac{\lambda}{\lambda_4}\right)^4\right] g(n_4'), \tag{23}$$

where

$$g(n_4') = \frac{\exp(-4n_4' \cot^{-1}\frac{1}{4}n_4')}{1-\exp(-2\pi n_4')}, \tag{24}$$

and

$$\lambda_4 = 16/(Z-s_4)^2 R_\infty, \quad n_4' = 4[\lambda/(\lambda_4-\lambda)]^{1/2}. \tag{25}$$

About the validity of these formulas, the arguments given in connection with the *M* absorption hold even more closely. In order to estimate roughly the contribution of the *N* shell for $\lambda \ll \lambda_4$, we may use the asymptotic solutions:

$$\sigma_{4s}{}^{D} = \frac{2^{10}}{3} r_0 \lambda \left(\frac{\lambda}{\lambda_4}\right)^{5/2} \quad \text{and} \quad \sigma_{4p}{}^{D} = 5 \times 2^{10} r_0 \lambda \left(\frac{\lambda}{\lambda_4}\right)^{7/2}. \tag{26}$$

Numerical Calculations

In order to calculate absorption cross sections one has to know in the equation for

$$\lambda_n = n^2/(Z-s_n)^2 R_\infty$$

Slater's screening constant s_n for a particular element and electron shell. Theoretical values for s_n as function of the atomic number Z are given, e.g., in Ref. 30. About their determination from spectroscopic data see Refs. 31 and 32. We see from Eqs. (3a), (7a), (11a), etc., that $\sigma_{n,l}{}^{D}/\lambda$ is in all cases a function of λ/λ_n only. Their numerical values are compiled for the 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 3*d* electrons in Table I for the wavelength ratio within $0.001 < \lambda/\lambda_n \leq 1$.[33] By means of this table one can easily obtain the numerical values for the photoelectric absorption cross sections for all elements and wavelengths within the limits of the theory, provided that the screening constants are known.

Since the quadrupole or dipole-octupole terms have always the simple form

$$\sigma_{n,l}{}^{Q} \propto (\sigma_{n,l}{}^{D}/\lambda) f(\lambda/\lambda_n), \tag{27}$$

where $f(\lambda/\lambda_n)$ is a polynomial of λ/λ_n, it is easy to determine their contributions using the values for $\sigma_{n,l}{}^{D}/\lambda$ of Table I for a special ratio of λ/λ_n. For a substance containing one sort of atom only, the linear absorption coefficient is given by

$$\tau = N \sum_{n,l} z_{n,l}(\sigma_{n,l}{}^{D} + \sigma_{n,l}{}^{\alpha}), \tag{28}$$

where N is the number of atoms per cm^3 and $z_{n,l}$ is the number of electrons with the quantum number *n*, *l*.

The above calculations are based on the nonrelativistic approximation, which means, for the *K* shell, $Z^2\alpha^2 \ll 1$, and for all shells, $\lambda_c \ll \lambda$.[34] A further restriction to the above calculations is that the incident wavelength

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[29] Equations (25) and (26) together with (27) have been evaluated directly from Harriman's results (Ref. 20).

[30] G. W. Grodstein, Natl. Bur. Std. (U. S.) Circ. 583 (1957), Table 1.

[31] A. Sommerfeld, *Atombau und Spektrallinien* (Frederick Vieweg and Sohn, Braunschweig, 1950), 2nd. ed., Vol. 1.

[32] A. E. Sandström, *Encyclopaedia of Physics* (Springer-Verlag, Berlin, 1957), Vol. 30.

[33] The calculations have been carried out by Miss J. Vierkant with a 'Zuse 23' electronic computer at the Institut für Theoretische Physik der Freien Universität Berlin. The author expresses his appreciation to the Institut für Theoretische Physik for permission to use the machine and to Miss J. Vierkant for carrying out the calculations.

[34] For the case $\lambda_c \sim \lambda$ F. Sauter (Ref. 13) calculated the photoelectric absorption cross section for the *K* shell. A rigorous relativistic calculation for the *K* and *L* shell was carried out by R. H. Pratt [Phys. Rev. **117**, 1017 (1960); **119**, 1619 (1960)].

TABLE I. Photoelectric dipole absorption cross section per electron (10^{-13} cm^2). The integers to the right of the entry are the powers of ten by which the entry should be multiplied.

λ/λ_n	σ_{1s}^D	σ_{2s}^D	σ_{2p}^D	σ_{3s}^D	σ_{3p}^D	σ_{3d}^D
0.001	0.1724−5	0.6258−5	0.6256−8	0.1279−4	0.4529−7	0.2271−10
0.002	0.9378	0.3272−4	0.6541−7	0.6441	0.4543−6	0.4567−9
0.003	0.2508−4	0.8497	0.2547−6	0.1626−3	0.1713−5	0.2590−8
0.004	0.5022	0.1660−3	0.6631	0.3103	0.4342	0.8775
0.005	0.8585	0.2777	0.1386−5	0.5088	0.8862	0.2245−7
0.006	0.1328−3	0.4214	0.2523	0.7583	0.1579−4	0.4811
0.007	0.1918	0.5979	0.4176	0.1059−2	0.2562	0.9128
0.008	0.2634	0.8080	0.6447	0.1409	0.3882	0.1585−6
0.009	0.3482	0.1052−2	0.9441	0.1810	0.5587	0.2572
0.010	0.4467	0.1330	0.1326−4	0.2259	0.7719	0.3958
0.020	0.2254−2	0.6002	0.1193−3	0.9237	0.6086−3	0.6382−5
0.030	0.5709	0.1400−1	0.4161	0.2011−1	0.1921−2	0.3081−4
0.040	0.1093−1	0.2507	0.9910	0.3412	0.4212	0.9166
0.050	0.1800	0.3896	0.1920−2	0.5070	0.7596	0.2099−3
0.060	0.2692	0.5540	0.3268	0.6941	0.1214−1	0.4083
0.070	0.3774	0.7419	0.5093	0.8992	0.1787	0.7103
0.080	0.5043	0.9511	0.7445	0.1120 0	0.2481	0.1140−2
0.090	0.6501	0.1180 0	0.1037−1	0.1353	0.3294	0.1721
0.100	0.8146	0.1427	0.1390	0.1598	0.4226	0.2477
0.110	0.9977	0.1690	0.1808	0.1852	0.5275	0.3431
0.120	0.1199 0	0.1968	0.2292	0.2116	0.6437	0.4605
0.130	0.1419	0.2261	0.2847	0.2387	0.7712	0.6021
0.140	0.1657	0.2566	0.3475	0.2664	0.9094	0.7700
0.150	0.1912	0.2884	0.4176	0.2948	0.1058 0	0.9662
0.160	0.2185	0.3212	0.4955	0.3237	0.1217	0.1193−1
0.170	0.2476	0.3551	0.5811	0.3531	0.1387	0.1451
0.180	0.2784	0.3900	0.6747	0.3829	0.1565	0.1744
0.190	0.3108	0.4258	0.7763	0.4131	0.1754	0.2072
0.200	0.3450	0.4623	0.8862	0.4436	0.1951	0.2438
0.210	0.3808	0.4997	0.1004 0	0.4744	0.2157	0.2842
0.220	0.4182	0.5378	0.1131	0.5056	0.2372	0.3287
0.230	0.4572	0.5765	0.1266	0.5370	0.2595	0.3774
0.240	0.4978	0.6159	0.1409	0.5686	0.2826	0.4304
0.250	0.5400	0.6559	0.1562	0.6004	0.3065	0.4879
0.260	0.5837	0.6964	0.1722	0.6325	0.3311	0.5499
0.270	0.6289	0.7374	0.1892	0.6647	0.3565	0.6166
0.280	0.6757	0.7789	0.2070	0.6970	0.3826	0.6882
0.290	0.7239	0.8208	0.2257	0.7295	0.4083	0.7647
0.300	0.7736	0.8632	0.2453	0.7622	0.4367	0.8462
0.310	0.8247	0.9059	0.2658	0.7949	0.4648	0.9328
0.320	0.8772	0.9490	0.2872	0.8278	0.4935	0.1025 0
0.330	0.9311	0.9924	0.3094	0.8607	0.5228	0.1122
0.340	0.9864	0.1036+1	0.3325	0.8938	0.5527	0.1224
0.350	0.1043+1	0.1080	0.3565	0.9269	0.5831	0.1333
0.360	0.1101	0.1124	0.3815	0.9601	0.6142	0.1446
0.370	0.1160	0.1169	0.4072	0.9934	0.6457	0.1565
0.380	0.1221	0.1214	0.4339	0.1027+1	0.6777	0.1690
0.390	0.1283	0.1259	0.4615	0.1060	0.7103	0.1821
0.400	0.1346	0.1304	0.4900	0.1093	0.7433	0.1958
0.410	0.1411	0.1349	0.5193	0.1127	0.7768	0.2100
0.420	0.1476	0.1395	0.5495	0.1160	0.8108	0.2249
0.430	0.1543	0.1440	0.5806	0.1194	0.8452	0.2403
0.440	0.1611	0.1486	0.6126	0.1227	0.8800	0.2564
0.450	0.1681	0.1532	0.6455	0.1261	0.9153	0.2731
0.460	0.1751	0.1578	0.6792	0.1295	0.9509	0.2904
0.470	0.1823	0.1624	0.7138	0.1328	0.9870	0.3083
0.480	0.1895	0.1671	0.7493	0.1362	0.1023+1	0.3268
0.490	0.1969	0.1717	0.7857	0.1395	0.1060	0.3460
0.500	0.2044	0.1763	0.8229	0.1429	0.1097	0.3658
0.510	0.2120	0.1810	0.8610	0.1462	0.1135	0.3862
0.520	0.2197	0.1856	0.9000	0.1496	0.1173	0.4073
0.530	0.2275	0.1903	0.9398	0.1530	0.1211	0.4290
0.540	0.2355	0.1950	0.9805	0.1563	0.1249	0.4514
0.550	0.2435	0.1996	0.1022+1	0.1597	0.1288	0.4744
0.560	0.2516	0.2043	0.1064	0.1630	0.1327	0.4981
0.570	0.2598	0.2090	0.1108	0.1664	0.1366	0.5224
0.580	0.2682	0.2136	0.1152	0.1697	0.1406	0.5474
0.590	0.2766	0.2183	0.1197	0.1731	0.1446	0.5731
0.600	0.2851	0.2230	0.1242	0.1764	0.1486	0.5994
0.610	0.2937	0.2276	0.1289	0.1798	0.1526	0.6263
0.620	0.3024	0.2323	0.1336	0.1831	0.1567	0.6540

TABLE I (*continued*)

λ/λ_n	$\sigma_{1s}{}^D$	$\sigma_{2s}{}^D$	$\sigma_{2p}{}^D$	$\sigma_{3s}{}^D$	$\sigma_{3p}{}^D$	$\sigma_{3d}{}^D$
0.630	0.3112+1	0.2370+1	0.1384+1	0.1864+1	0.1608+1	0.6823 0
0.640	0.3201	0.2416	0.1434	0.1898	0.1649	0.7113
0.650	0.3291	0.2463	0.1483	0.1931	0.1690	0.7409
0.660	0.3382	0.2510	0.1534	0.1964	0.1732	0.7712
0.670	0.3473	0.2556	0.1586	0.1998	0.1774	0.8022
0.680	0.3566	0.2603	0.1638	0.2031	0.1815	0.8339
0.690	0.3659	0.2649	0.1691	0.2064	0.1858	0.8663
0.700	0.3753	0.2696	0.1745	0.2097	0.1900	0.8993
0.710	0.3848	0.2742	0.1800	0.2130	0.1942	0.9330
0.720	0.3944	0.2788	0.1855	0.2163	0.1958	0.9673
0.730	0.4040	0.2835	0.1911	0.2196	0.2028	0.1002+1
0.740	0.4137	0.2881	0.1969	0.2229	0.2071	0.1038
0.750	0.4236	0.2927	0.2026	0.2262	0.2114	0.1075
0.760	0.4334	0.2973	0.2085	0.2295	0.2157	0.1112
0.770	0.4434	0.3019	0.2144	0.2328	0.2201	0.1149
0.780	0.4535	0.3065	0.2205	0.2361	0.2244	0.1188
0.790	0.4636	0.3111	0.2266	0.2394	0.2288	0.1227
0.800	0.4738	0.3157	0.2327	0.2426	0.2332	0.1267
0.810	0.4840	0.3203	0.2390	0.2459	0.2376	0.1307
0.820	0.4944	0.3248	0.2453	0.2492	0.2420	0.1348
0.830	0.5048	0.3294	0.2517	0.2524	0.2464	0.1390
0.840	0.5152	0.3339	0.2582	0.2557	0.2509	0.1433
0.850	0.5258	0.3385	0.2647	0.2589	0.2553	0.1476
0.860	0.5364	0.3430	0.2714	0.2622	0.2598	0.1520
0.870	0.5471	0.3475	0.2781	0.2654	0.2642	0.1565
0.880	0.5578	0.3520	0.2848	0.2686	0.2687	0.1610
0.890	0.5687	0.3565	0.2917	0.2719	0.2732	0.1656
0.900	0.5795	0.3610	0.2986	0.2751	0.2777	0.1702
0.910	0.5905	0.3655	0.3056	0.2783	0.2822	0.1750
0.920	0.6015	0.3700	0.3126	0.2815	0.2867	0.1798
0.930	0.6126	0.3745	0.3198	0.2847	0.2912	0.1846
0.940	0.6237	0.3789	0.3270	0.2879	0.2958	0.1896
0.950	0.6349	0.3834	0.3343	0.2911	0.3003	0.1946
0.960	0.6462	0.3878	0.3416	0.2943	0.3048	0.1996
0.970	0.6575	0.3922	0.3490	0.2975	0.3094	0.2048
0.980	0.6889	0.3967	0.3565	0.3007	0.3139	0.2100
0.990	0.6803	0.4011	0.3641	0.3039	0.3185	0.2152
1.000	0.6905	0.4040	0.3703	0.3053	0.3231	0.2193

must not be just below the absorption edge wavelength. We did not consider the influence of the Compton effect. This can be done using the formula derived by Klein and Nishina.[35]

There seems to be quite good agreement between experimental and theoretical data. Measured values for germanium by Hildebrandt[9] are compared with the theoretical data in Table II. For the numerical calculations we have used screening constants obtained from spectroscopic data.

TABLE II. Measured and calculated linear absorption coefficients for germanium.

Radiation	λ (Å)	Experiment τ	Theory $\tau=\tau^D+\tau^Q$	τ^D	τ^Q
Ag $K\alpha$	0.56	168 (Hildebrandt)[a] 171[b]	174	167.2	6.7
Mo $K\alpha$	0.71	321 (Hildebrandt)[a] 319 (Batterman)[c]	329	321.6	8.3
Cu $K\alpha$	1.54	350 (Hildebrandt)[a] 353 (Bonse)[c] 352 (Batterman)[c]	339	330.8	7.7
Fe $K\alpha$	1.94	638 (Hildebrandt)[a]	653	641.4	11.4

[a] See Ref. 9. [b] See Ref. 10. [c] See Ref. 39.

B. PHOTOELECTRIC ABSORPTION OF X RAYS IN THE CASE OF THE BORRMANN EFFECT

In order to consider the scattering of x rays within perfect single crystals of refractive index $n^2=\epsilon$ (ϵ = electrical permittivity), it is necessary to use the so-called 'dynamical theory of x-ray diffraction,' which in different formulations is due to Darwin and Ewald. Later Laue reformulated the theory and his approach is used nowadays.[36] Since the refractive index is nearly one for x rays, one obtains for the electrical susceptibility:

$$4\pi\chi=\epsilon-1\simeq 2(n-1)\,. \tag{29}$$

For x-ray energies high compared with the energies of the bound electron states, one obtains

$$\chi(\mathbf{r})=-4\pi r_0\rho(\mathbf{r})/K^2\,. \tag{30}$$

$\rho(\mathbf{r})$ is the electron charge density of the crystal, and $K=2\pi/\lambda$ is the vacuum wave number of the x rays.

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[35] O. Klein and Y. Nishina, Z. Physik **52**, 853 (1929).

[36] The dynamical theory was recently discussed in a review article by P. P. Ewald [Rev. Mod. Phys. **37**, 47 (1965)].

Since χ and ρ have the periodicity of the crystal lattice, one can use the following Fourier representation for χ:

$$\chi(\mathbf{r})=\sum_h \chi_h \exp(-2\pi i\mathbf{h}\cdot\mathbf{r})$$

with

$$\chi_h=\frac{1}{V}\int_{\text{crystal cell}} \chi \exp(2\pi i\mathbf{h}\cdot\mathbf{r})d\tau\,, \tag{31}$$

where $\mathbf{h}=h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3$ is a reciprocal lattice vector, and V is the volume of the crystal unit cell. Inserting (31) in the wave equation

$$\nabla^2\mathbf{E}-\frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}=-4\pi \text{ curl curl}\mathbf{P}$$

leads directly to Laue's dynamical theory. It is obvious that the solutions of this wave equation have Bloch-wave character. If absorption has to be considered, n becomes complex and hence so does χ, but it still remains periodic within the crystal lattice. This function was treated within the framework of the dynamical theory by Molière.[4] Molière discussed the theory for the region where the Kronig fine structure of the absorption becomes important (i.e., if the wavelength of the x rays is close to and below the corresponding wavelength of an absorption edge). He therefore used Bloch waves for the emitted electrons. Unfortunately, Molière's formulas are difficult to handle for any sort of practical calculations. On the other hand, outside this region it seems to be a good approximation to use for the 'free' electrons hydrogen-like wave functions, as in Sec. A of this paper. If we assume that the x rays within the crystal fulfill Bragg's condition for only one lattice plane, then we obtain for the corresponding imaginary part of the Fourier coefficient[3,37]:

$$\chi_{ih}=(N_c/K)D_h\sum_A \sigma_A(\theta_3,\lambda)\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}_A)\,, \tag{32}$$

where N is the number of crystal unit cells per cm^3 and $D_h=e^{-M}$ is the Debye-Waller factor for this reflection. The summation has to be carried out over all atoms within the unit cell. $\mathbf{r}_A$ is a position vector for the Ath atom in the unit cell. $\sigma(\theta_B,\lambda)$ is an angular-dependent absorption cross section:

$$\sigma_A=\frac{8\pi^2e^2\hbar^2}{m^2c^2K}\sum_{l',m'}\sum_{n,l,m}\langle\rho'|\nabla\cdot\mathbf{E}_0e^{i\mathbf{K}\cdot\mathbf{r}}|\rho\rangle \times\langle\rho|\nabla\cdot\mathbf{E}_he^{-i\mathbf{K}_h\cdot\mathbf{r}}|\rho'\rangle. \tag{33}$$

$\sigma_A(\theta_B,\lambda)$ depends on the polarization direction of the x rays and the Bragg angle Θ_B which is given by the equation $|\mathbf{K}_h-\mathbf{K}|=2\pi h=4\pi\sin\Theta_B/\lambda$, where $\mathbf{K}_h=\mathbf{K}+2\pi\mathbf{h}$, and $\mathbf{E}_0$ and $\mathbf{E}_h$ are unit vectors of the electric field strength corresponding to the two waves with wave vectors $\mathbf{K}$ and $\mathbf{K}_h$, respectively. For $\mathbf{K}=\mathbf{K}_h$, and hence $\mathbf{E}_0=\mathbf{E}_h$, Eq. (33) is identical with Eq. (2). This, in conjunction with (32), leads directly to χ_{i0}. If the crystal contains only one species of atoms, one obtains

$$\chi_{i0}=(N/K)\sigma_A=\tau/K\,, \tag{34}$$

where N is the number of atoms per cm^3 and $\tau=N\sigma_A$ is the linear absorption coefficient of the substance. In the abovementioned paper (Ref. 3) we introduced the Debye-Waller factor without any theoretical proof. Recently Ohtsuki[5] has given a rigorous derivation of Eq. (32). The calculation of the integrals in (33) becomes, if one uses Hönl's approach,[21] for $\mathbf{K}\neq\mathbf{K}_h$, relatively simple. The retardation factors $e^{i\mathbf{K}\cdot\mathbf{r}}$ and $e^{i\mathbf{K}_h\cdot\mathbf{r}}$ are expanded in a Taylor series. Hönl chooses the propagation directions of $\mathbf{K}$ and $\mathbf{K}_h$ as polar axes $x=r\cos\vartheta$ and $\xi=r\cos\Theta$ of two Cartesian coordinate systems which are rotated with respect to each other, such that the angle between $\mathbf{K}$ and $\mathbf{K}_h$ is identical with the scattering angle (i.e., twice the Bragg angle). $\mathbf{E}_0$ is identical with the y axis of the first system, but for $\mathbf{E}_h$ we have according to the two-beam case in the dynamical theory two possibilities. Either $\mathbf{E}_h$ lies perpendicular to $\mathbf{K}$ and $\mathbf{K}_h$ and hence parallel to $\mathbf{E}_0$ or all four vectors are lying in one plane. For the two cases one obtains different values for (33), which we denote for the first case by $\sigma_A{}^{\perp}$ (i.e., $\mathbf{E}_0$ parallel $\mathbf{E}_h$) and in the second case by $\sigma_A{}^{\parallel}$. The corresponding expressions for χ_{ih} are called $\chi_{ih}{}^{\perp}$, and $\chi_{ih}{}^{\parallel}$. According to Hönl's[21] and Eisenlohr's and Müller's[22] results for the anomalous dispersion correction for the atomic scattering factor, every multipole has its own angular dependence. This calculation can be applied directly to our problem If we introduce in Hönl's Eqs. (16a) and (16b) the values $\alpha=\frac{1}{2}\pi$, $\vartheta_0=2\theta_B$ for the first polarization direction, then we obtain

$$\sigma_A{}^{\perp}=(\sigma_A{}^D+\sigma_A{}^{D,O})+\sigma_A{}^Q\cos2\theta_B. \tag{35}$$

For the second polarization direction we have to choose $\alpha=\pi$, $\vartheta_0=2\theta_B$ and obtain

$$\sigma_A{}^{\parallel}=(\sigma_A{}^D+\sigma_A{}^{D,O})\cos2\theta_B+\sigma_A{}^Q\cos4\theta_B. \tag{36}$$

This angular dependence is the same for all atomic electrons, hence we have

$$\sigma_A{}^D=\sum_i\sigma_i{}^D;\quad \sigma_A{}^{D,O}=\sum_i\sigma_i{}^{D,O};\quad \sigma_A{}^Q=\sum_i\sigma_i{}^Q, \tag{37}$$

where the summation i has to be carried out over all electrons of the atom. $\sigma_i{}^D$, $\sigma_i{}^{D,O}$, $\sigma_i{}^Q$ are the absorption cross sections corresponding to the dipole, dipole-octupole, and quadrupole terms, which are given in Sec. A of this paper. Since $\sigma_A{}^Q\ll\sigma_A{}^D$ (cf. Table II), $\sigma_A{}^{\perp}$ shows even for large Bragg angles a small angular dependence though this is not the case for $\sigma_A{}^{\parallel}$, which is strongly angular-dependent. It is possible to measure $\chi_{ih}{}^{\perp}$ directly in an appropriate thick prefect single crystal by means of the Borrmann effect.[2] A simple method was presented

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[37] Apart from the Debye-Waller factor this equation follows from Molière's (Ref. 4) Eq. (5.8) by replacing the Bloch functions by hydrogen-like eigenfunctions of the continuous spectrum, then the electron wave vector **k** is spherically symmetric in the k space and Eq. (32) together with (33) follows straight on. Compare as well Eq. (40) in Ohtsuki's paper (Ref. 5).

at first by Borrmann.[38] Accurate measurements for germanium have been carried out by a number of authors.[7–9,39] For this lattice $\chi_{ih}{}^{\perp}$ has the value

$$\chi_{ih}{}^{\perp}=(a_hD_h/K)\tau^{\perp}(\theta_B,\lambda)=(a_hD_h/K)(\tau^D+\cos 2\theta_B\tau^Q) \quad (38)$$

and $\chi_{ih}{}^{\parallel}$ has the value

$$\chi_{ih}{}^{\parallel}=\frac{a_hD_h}{K}\tau^{\parallel}(\theta_B,\lambda)=\frac{a_hD_h}{K}(\cos 2\theta_B\tau^D+\cos 4\theta_B\tau^Q), \quad (39)$$

where $\tau^D=N(\sigma_A{}^D+\sigma_A{}^{D,O})$, $\tau^Q=N\sigma_A{}^Q$ (N is the number of atoms per cm^3), and a_h is a geometrical factor. $a_h=1$ if h_1, h_2, h_3 all even and $(h_1+h_2+h_3)/4$ integer; $a_h=1/\sqrt{2}$, if h_1, h_2, h_3 all odd and $a_h=0$ otherwise. By means of the Borrmann effect one determines the quantity

$$\eta_h=(\chi_{ih}{}^{\perp}/\chi_{i0})=D_ha_h(1-2\sin^2\theta_B\tau^Q/\tau), \quad (40)$$

where $\tau=\tau^D+\tau^Q$ is the linear photoelectric absorption coefficient, which can be directly determined from normal absorption measurements. Since the Debye-Waller factor is a function of $\sin\theta/\lambda$ one obtains by measuring (40) for the same reflection but two different wavelengths:

$$q_h=\frac{\eta(\lambda_1)}{\eta(\lambda_2)}=\frac{1-2\sin^2\theta_1[\tau^Q(\lambda_1)/\tau(\lambda_1)]}{1-2\sin^2\theta_2[\tau^Q(\lambda_2)/\tau(\lambda_2)]}. \quad (41)$$

TABLE III. Comparison between experimental and theoretical data (Ref. 9) for $q_h=\rho_h(\lambda_1)/\rho_h(\lambda_2)$ where $\lambda_1=0.71$ Å and $\lambda_2=1.54$ Å.

Reflection	q_h (Experiment)	q_h (Theory)
220	1.005±0.002	1.005
400	1.010±0.005	1.010
422	1.013±0.008	1.015
440	1.019±0.013	1.020
444	1.048±0.020	1.031

Any deviation of q_h from one is caused by electrical quadrupole transitions. Hildebrandt[9] has measured η_h in germanium for different reflections h and different wavelength. The results are given in Table III, for $\lambda_1=0.71$ Å (Mo $K\alpha$ radiation) and $\lambda_2=1.54$ Å (Cu $K\alpha$ radiation) in terms of the quantities q_h. The agreement with the theoretical results is fairly good. The results indicate clearly the existence of electrical quadrupole transitions. By measuring the linear absorption coefficient, together with accurate measurements of η_h, for two different wavelengths λ and two reflections $h=h_1$, h_2, h_3 and $g=g_1$, g_2, g_3, one can determine τ^Q experimentally. From Eq. (41) we obtain, e.g.

$$\tau^Q(\lambda_2)=\frac{\tau(\lambda_2)}{2}\cdot\frac{(1-q_h)\sin^2\theta_3-(1-q_g)\sin^2\theta_1}{\sin^2\theta_1\sin^2\theta_4q_g-\sin^2\theta_2\sin^2\theta_3q_h}, \quad (42)$$

where Θ_1, Θ_3 are the Bragg angles corresponding to the two reflections h and g and the wavelength λ_1 and Θ_2, Θ_4 are the other two Bragg angles for the wavelength λ_2. If we know τ^Q and τ accurately, then we can determine the Debye-Waller factor from Eq. (40). Hence the Borrmann effect allows in principle a direct determination of the Debye-Waller factor.

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