ANOMALOUS TRANSMISSION OF X-RAYS IN GERMANIUM

PART I: THE IMAGINARY PART OF THE ATOMIC SCATTERING FACTOR

by B. OKKERSE

Summary
The coefficient of absorption for X-rays transmitted anomalously through thick, perfect crystals is \((1 - \epsilon_H)\) times smaller than the absorption coefficient for normal transmission. The absolute value and the temperature dependence of \((1 - \epsilon_H)\) have been determined in germanium with Cu Ka radiation for the (220), (400) and (422) reflexions. On the basis of a simple physical picture the relation between the values of \((1 - \epsilon_H)\) for different reflexions may be understood. The Debije temperature may be derived from the temperature dependence of \((1 - \epsilon_H)\) as 294 ± 5 °K. The results are compared with those obtained by other authors.

Résumé
Le coefficient d'absorption pour les rayons X transmis anormalement à travers un cristal épais et parfait est \((1 - \epsilon_H)\) fois plus petit que le coefficient d'absorption pour la transmission normale. La valeur absolue de \((1 - \epsilon_H)\) et sa variation en fonction de la température ont été déterminées dans le germanium avec la raie Cu Ka pour les réflexions (220), (400) et (422). On peut comprendre la relation entre les valeurs de \((1 - \epsilon_H)\) pour différentes réflexions grâce à un simple modèle physique. La variation de \((1 - \epsilon_H)\) en fonction de la température permet de déterminer la température de Debije comme étant 294 ± 5 °K. Les résultats sont comparés avec ceux obtenus par d'autres auteurs.

Zusammenfassung
Der Absorptionskoeffizient von Röntgenstrahlen ist im Falle der Interferenz bei dicken idealen Kristallen um einen Faktor \((1 - \epsilon_H)\) kleiner als der normale Absorptionskoeffizient. Der absolute Wert und die Temperaturabhängigkeit von \((1 - \epsilon_H)\) werden für Germanium mit der Cu Ka-Strahlung der (220)-, (400)- und (422)-Reflexe bestimmt. Unter Benutzung eines einfachen physikalischen Modells läßt sich die Beziehung zwischen den Werten von \((1 - \epsilon_H)\) für verschiedene Reflexe verstehen. Die Debije-Temperatur kann aus der Temperaturabhängigkeit von \((1 - \epsilon_H)\) ermittelt werden, und zwar ergibt sich \(\Theta_D = 294 ± 5 °K\). Die Ergebnisse werden mit denjenigen anderer Autoren verglichen.

1. Introduction
The availability of man-made nearly perfect crystals has in recent years stimulated much investigation into the dynamical theory of X-ray diffraction. One of the consequences of the dynamical interaction between X-rays and the lattice is the phenomenon of anomalous transmission of X-rays, discovered by Borrmann 1) and theoretically explained by Von Laue 2), Hirsch 3) and Zachariasen 4). This anomalous transmission has been used, among other
things, to investigate the effect of elastic deformation of the lattice on the diffraction of X-rays. Up till now the lattice has been deformed by elastic mechanical bending (Hunter 5), Cole and Brock 6), Okkerse 7) or by temperature gradients (Borrmann and Hildebrandt 8), Okkerse 7)). The effect has been treated theoretically by Borrmann and Hildebrandt 8) and, more generally, by Penning and Polder 9).

In the course of an experimental investigation into the effect of temperature gradients on the anomalous transmission of X-rays in dislocation-free germanium crystals it proved necessary to determine the temperature dependence of the anomalous transmission. This work led us to investigate in more detail the important parameter $\epsilon_H$ of the anomalous transmission.

2. Theoretical considerations

Quantitative expressions for the diffracted intensities have been derived by Von Laue 2), Zachariasen 4) and Hirsch 3) on the basis of the dynamical theory. For the symmetrical Laue case (see fig. 1) Hirsch obtained for the reflected intensity:

$$\frac{I_R(y)}{I_0} = \exp \left[ -\mu_0 l \left( 1 - \epsilon_H' \sqrt{1 + y^2} \right) / (1 + y^2) \right], \quad (1)$$

and for the transmitted intensity:

$$\frac{I_T(y)}{I_0} = \exp \left[ -\mu_0 l \left( 1 - \epsilon_H' \sqrt{1 + y^2} \right) (y - \sqrt{1 + y^2})^2 / (1 + y^2) \right], \quad (2)$$

where

- $\mu_0$ is the linear absorption coefficient of the X-rays used,
- $l$ is the thickness of the crystal in the direction of the X-ray beam,
- $\epsilon_H'$ is $K(F_{H''}/F_0'')$,
- $K$ is the polarization factor,
- $F_{H''}$ is the imaginary part of the structure factor for the $(hkl)$ reflexion,
- $F_0''$ is the imaginary part of the structure factor for the transmitted beam,
- $y$ is $(\theta_B - \theta) \sin 2\theta_B CKF_{hkl}$,
- $C$ is $4\pi e^2/m\omega_0^2V$, $e$ and $m$ being the charge and mass of the electron, respectively $\omega_0$ the circular frequency of the X-rays, and $V$ the volume of the unit cell.
- $F_{hkl}$ is the structure factor for the $(hkl)$ reflexion.

Fig. 1. Symmetrical Laue case.
Equations (1) and (2) are valid for \(0.75 < \epsilon_H' < 1.00\) and \(\mu_0 l > 10\). In practice only integrated intensities are measured. The expressions (1) and (2) can be expanded and integrated in series:

\[
\frac{I_R(y)}{I_0} = \sqrt{\frac{\pi}{8}} \frac{\exp \left[ -\mu_0 l (1-\epsilon_H') \right]}{\sqrt{a}} \left( 1 + \frac{1}{8a} + \frac{0.0703}{a^2} + \ldots \right),
\]

\[
\frac{I_T(y)}{I_0} = \sqrt{\frac{\pi}{8}} \frac{\exp \left[ -\mu_0 l (1-\epsilon_H') \right]}{\sqrt{a}} \left( 1 + \frac{17}{8a} + \frac{5.32}{a^2} + \ldots \right),
\]

where \(a = \epsilon_H' \mu_0 l\).

Experimentally the integrated intensity is measured by slowly rotating the crystal through the Bragg angle. Transformation of eqs (3) and (4) from the \(y\)-scale to the \(\theta\)-scale yields

\[
\frac{I_R}{I_0} = \frac{CKF_{hkl}}{\sin 2\theta_B} \sqrt{\frac{\pi}{8}} \frac{\exp \left[ -\mu_0 l (1-\epsilon_H') \right]}{\sqrt{a}} \left( 1 + \frac{1}{8a} + \frac{0.0703}{a^2} + \ldots \right),
\]

\[
\frac{I_T}{I_0} = \frac{CLF_{hkl}}{\sin 2\theta_B} \sqrt{\frac{\pi}{8}} \frac{\exp \left[ -\mu_0 l (1-\epsilon_H') \right]}{\sqrt{a}} \left( 1 + \frac{17}{8a} + \frac{5.32}{a^2} + \ldots \right).
\]

Equations (5) and (6) are valid for the two main directions of polarization. For the wave field with the electric-field vector in the reflecting planes we have \(K = 1\) and \(\epsilon_H' = \epsilon_H\), for the wave field with the magnetic-field vector in the reflecting planes the corresponding values are \(K = \cos 2\theta_B\) and \(\epsilon_H' = \epsilon_H \cos 2\theta_B\).

In sufficiently thick specimens the contribution of the second wave field may be neglected, and the integrated intensities are given by eqs (5) and (6) with \(K = 1\) and \(\epsilon_H' = \epsilon_H\).

In the derivation of eqs (1) and (2) the important parameter \(\epsilon_H\) has been introduced in a formal way. Its meaning may be more clearly understood by means of the following reasoning. The electromagnetic energy is proportional to \(|\mathbf{E}|^2\), whereas the energy absorbed is proportional to \(\epsilon''|\mathbf{E}|^2\), where \(|\mathbf{E}|\) is the local magnitude of the electric-field vector and \(\epsilon''\) is the local imaginary part of the dielectric constant. Thus, in a lattice with spacing \(d\) (see fig. 2):

\[
I = a \int_0^d |\mathbf{E}|^2 \, dx,
\]

and

\[
-\frac{dI}{dz} = \beta \int_0^d \epsilon'' |\mathbf{E}|^2 \, dx.
\]

The absorption coefficient in the direction of the incident beam is therefore given by
Far from the Bragg angle only one plane wave, with wave vector $k$, predominates: $E = E_0 \exp(jk \cdot r)$.

Equation (7) reduces to

$$\mu = -\frac{1}{I} \frac{d\beta}{dz} = \frac{\beta}{\alpha} \int_0^d e'' |E|^2 dx = \beta \frac{e''}{\alpha} = \mu_0,$$  \hspace{1cm} (7)$$

where $\mu_0$ is the normal absorption coefficient.

In the case of Bragg reflexion two plane-wave components predominate, with wave vectors of $k$ and $(k - 2b)$ respectively, where $2b$ is $2\pi$ times the reciprocal lattice vector, and

$$E = E_0 [\exp(jk \cdot r) + \xi \exp\{j(k - 2b) \cdot r\}],$$

$\xi$ is the ratio in amplitude of the two plane-wave components. In this case

$$|E|^2 = |E_0|^2 (1 + \xi^2 + 2\xi \cos 2b \cdot r).$$

Now $e''$ is zero except very near to the atomic planes, because the absorption mainly takes place through the inner electrons of the atoms and the amplitude of the atomic vibrations is small. Therefore $e'' \cos 2b \cdot r$, which in our case is equal to $e'' \cos 2b \cdot x$, may be approximated by $e''(1 - 2b^2 x^2)$. After some algebraic computation eq. (7) reduces to

$$\frac{\mu}{\mu_0} = 1 + \frac{2\xi}{1 + \xi^2} \epsilon_H$$ \hspace{1cm} (9)$$

with

$$1 - \epsilon_H = \frac{2\pi^2 n^2}{d^2} \int_0^d e'' x^2 dx / d \epsilon''.$$ \hspace{1cm} (10)$$

where $n$ is the order of the reflexion.

If the displacement of all atoms perpendicular to the lattice plane were $u$, then
On the average for lattice vibrations $\bar{u} = 0$ so that

$$1 - \epsilon_H = \frac{2\pi^2 n^2}{d^2} \left[ \int_0^d \epsilon''(p) (u + p)^2 \, dp \right].$$

where $A$ is the absorption cross-section of the atom. From eq. (11) two conclusions may be drawn: first, $1 - \epsilon_H$ should be proportional to $n^2/d^2$, or, for cubic lattices, to $n^2(h^2 + k^2 + l^2) = H^2 + K^2 + L^2 = \Sigma H^2$, provided $\bar{u}^2$ is the same in all directions.

Secondly, $1 - \epsilon_H$ is a function of temperature through $\bar{u}^2$. According to the theory of Debije and Waller (see James 11): 

$$\bar{u}^2 = \frac{3 h^2}{M k \theta_D^2} \left\{ \phi(x) + \frac{x}{4} \right\},$$

where $M$ is the atomic mass, $\theta_D$ the Debije temperature, $x = \theta_D / T$, and $\phi(x) + x/4$ is a tabulated function. For the temperature interval used in our experiments $\bar{u}^2$ may be approximated by a linear function of temperature:

$$\bar{u}^2 = \frac{3h^2}{M k} (c + \gamma T),$$

where $c$ is a constant and $\gamma$ the temperature coefficient. Moreover, according to Debije and Waller:

$$F_H(T) = F_H \exp (-2\pi^2 n^2 \bar{u}^2 / d^2).$$

Combining eqs (6), (11), (13) and (14) one obtains for the temperature dependence of the integrated transmitted intensity:

$$I_T(T) = \text{const.} \exp \left[ -\frac{2\pi^2 n^2}{d^2} \left( \frac{1}{2} + \mu_0 l \right) \frac{3h^2}{M k} \gamma T \right] = \text{const.} \exp (-\alpha T),$$

in which equation the temperature dependence of $d$, $\theta_D$ and $l$ has been neglected, and $\alpha$ depends on the reflection and on the thickness of the specimen. A similar expression is found for the temperature dependence of the integrated reflected intensity.

Combining eqs (11) and (13) one obtains for the temperature dependence of $\epsilon_H$:

$$\frac{d \epsilon_H}{dT} = \frac{2\pi^2 n^2}{d^2} \frac{3h^2}{M k} \gamma.$$
3. Experimental part

3.1. Specimen preparation

The specimens used were cut from dislocation-free germanium crystals grown in the [110]-orientation by the method described in a previous paper \(^{12}\). The absence of dislocations was proved by the etch-pit method \(^{13}\) and by a photographic X-ray technique suggested by Barth and Hosemann \(^{14}\) (details of the method used are given in a forthcoming paper \(^{15}\)).

The specimens, either slabs or wedge-shaped samples, were sawn from the crystals with a diamond saw. The specimens were then lapped on abrasive powder, during which process the specimens were properly oriented. The orientation was measured on an X-ray goniometer. After a final lapping the specimens were etched in superoxol (10 ml H\(_2\)O\(_2\) 30\%, 9 ml HF 50\%, 1 ml destilled water, cold). During the lapping process more than 300 microns was removed and during the etching process there was a further removal of about 30 microns (by means of the above-mentioned photographic X-ray method it was verified that all surface damage had been removed). In this way it was possible to control the orientation of the reflecting planes with respect to the front and the back surface of the specimen to better than 0·05°. The tapering angle of the symmetric wedges was 2·00° for the (220)-wedge, 1·88° for the (400)-wedge and 0·97° for the (422)-wedge. The deviation in orientation of the reflecting planes with respect to the front and the back surface of the slabs used for measuring the temperature dependence was in all cases less than 0·05°. The deviation in orientation of the reflecting planes with respect to the long axis of the specimen was always less than 0·5°. The thickness of the specimens was measured with a micrometer; the inaccuracy was estimated to be less than 2 microns.

In order to heat a specimen small furnaces, consisting of three or four windings of "coax" copper-constantan thermocouple cable, were mounted at both ends of the slab, the constantan core of the cable being the heating wire. The temperature of each furnace was independently regulated by means of a "Chromel-Alumel" thermocouple and a temperature recorder and controller. The cold junctions of the thermocouples were kept in melting ice. The leads of the thermocouples were led through the furnaces to avoid heat losses from the hot junctions. In order to ensure good thermal contact the furnaces and the thermocouple junctions were soldered to the specimen, which at these places had been copper plated. A schematic diagram of a specimen, showing typical dimensions, is given in fig. 3. The specimen was clamped at the top furnace to the specimen holder and the light-weight electrical leads were glued to the specimen holder. Extreme care was taken in mounting the specimens in order to avoid elastic deformation \(^?\).
3.2. Temperature measurements

The thermocouple-recorder-controller system was calibrated in the temperature range of 25 to 100 °C against a calibrated thermometer by immersing the completely mounted specimens in a thermostat. It is believed that the calibration was correct to 0.1 °C. Because of heat transfer by convection and radiation from the surface of the specimen to the surroundings, the temperature of the specimen is not homogeneous, even if both furnaces are at the same temperature. The most general expression for the temperature distribution is given by Carslaw and Jaeger. When the proper data is inserted, it is found that at 100 °C the cross-sectional temperature gradients are still negligibly small. Also, in an analogous experiment with brass and lead specimens (the heat conductivity coefficients and presumably also the heat-transfer coefficients of these materials are close to those of germanium) no temperature difference between the interior and the surface could be detected. Neglecting the cross-sectional temperature gradients it can readily be shown that the temperature in the specimen is given by

\[ t = C_1 \exp(-mx) + C_2 \exp(mx) \]  

where \( m = \sqrt{hS/\pi B} \), \( t \) is the reduced temperature \( t = T - T_{\text{room}} \) at location \( x \), \( \pi \) the thermal conductivity, \( h \) the heat-transfer coefficient, \( S \) the cross-section and \( B \) the circumference of the specimen; the constants \( C_1 \) and \( C_2 \) depend on the boundary conditions. If the distance between the hot junctions is \( D \), and if the reduced temperature of the couples \( U \) and \( L \) (see fig. 3) is \( t_U \) and \( t_L \), respectively, then the reduced temperature halfway between the couples is given by

\[ t = \frac{1}{2}(t_U + t_L)/\cosh \left( \frac{1}{2} mD \right) \]  

and the temperature gradient by
\[
\frac{dT}{dx} = \frac{dt}{dx} = \frac{1}{2} \frac{m(t_u-t_L)}{\sinh \left( \frac{1}{2} mD \right)}.
\]  

(19)

In the literature, values for the heat-transfer coefficient are cited which vary from \(10^{-4}\) to \(3.10^{-4}\) cal/cm\(^2\) °C sec. By heating only one of the furnaces and recording the temperature difference between the two thermocouples, the heat-transfer coefficient was determined under experimental conditions. Using eq. (17) with the proper boundary conditions, and taking \(x = 0.134\) cal/cm°C sec, the best fit of the experimental data was obtained with \(h = 5.56.10^{-4}\) cal/cm\(^2\) °C sec. This relatively high value may be attributed to the forced convection stimulated by the furnaces. One can easily verify that an error of 10% in the ratio of \(h\) and \(x\) results in an error in the temperature of \(0.2\) °C at 100 °C under typical experimental conditions. The maximum inaccuracy in the temperatures calculated should therefore vary from about 0.5 °C at room temperature to about 1.0 °C at 100 °C.

3.3. X-ray equipment

The experimental arrangement is very similar to that described by Hunter \(^5\), except that no monochromator was used. The X-ray generator used was a standard Philips PW 1010 with a copper X-ray tube, of which the projected point source of \(1 \times 1\) mm\(^2\) was used. The operating voltage was in all experiments 26 kV. At this tube voltage the ratio of the characteristic radiation to the continuous radiation is still very favorable. The intensity of higher harmonics is negligible, as was verified by experiments at 17 kV. The slit system collimated the X-ray to a beam with a cross-section of \(1.5 \times 0.2\) mm\(^2\) at the site of the specimen. The counter and the specimen holder could be rotated about the axis of the goniometer, which axis was perpendicular to the vertical plane through the centre of the X-ray beam. The sample was mounted in such a way that the back surface of the specimen (exit plane for the X-rays) coincided with the axis of the goniometer. In this way the transmitted and reflected intensities are counted with equal counter sensitivity, provided the same region of the counter is used. For many purposes it was very useful that the specimen holder was constructed in such a way that the back surface of the crystal could be rotated and translated in two directions perpendicular to each other, while keeping the back surface of the sample in its own plane. The X-ray detector was a standard end-window Geiger tube. The X-ray tube current was always such that no dead-time correction was necessary. The counter slits, which were so wide that they just accommodated the diffracted beams, were used only while orienting the specimen. In order to measure the integrated intensity the specimen was rotated through an angle equal to twice the reflecting angle (which is for all practical purposes equal to the divergence of the incident beam). The measured intensity was corrected for background, which never amounted to
more than 3% of the total intensity. The irreproducibility in the integrated intensity due to the statistical error and variations in the rotation speed are of the order of 0.8 to 1.5%, depending on the counting rate.

4. Results

4.1. Determination of $\epsilon_H$ at constant temperature

According to eqs (5) and (6) $\epsilon_H$ can be obtained from measurements of the integrated intensity as a function of the thickness at constant temperature. Therefore the integrated intensity was measured as a function of the vertical position of a wedge-shaped specimen, in the same way as described by Hunter. In order to calibrate the thickness at one position a copper wire of 100 microns diameter was glued onto the specimen. A very sharp minimum in the plot of the integrated intensity versus vertical position indicated the position of the wire. At this location, corrected for the oblique angle of incidence, the thickness of the specimen was measured with a micrometer. The tapering angle can be obtained from thickness measurements at two locations. In all cases the tapering angle found in this way was the same as the angle obtained by X-ray measurements. The maximum error in the thickness was estimated to be about 2 microns; this was of no importance to the final result. Because the exponential part in eqs (5) and (6) varies much faster than the algebraic terms containing $\epsilon_H$, $\epsilon_H$ can be obtained from a plot of $\log I - \log \{\}$ versus thickness, where $\{\}$ stands for the algebraic terms. In a preliminary plot an estimated value for $\epsilon_H$ was used; in the final plot the values just obtained were used. The measurements were performed in an air-conditioned room, the temperature of which was recorded and found to have varied about 1°C in the course of the work; the average temperature was taken as the temperature of measurement. For $\mu_0$ the value of 352 cm$^{-1}$ is used. The result obtained for the (220), (400) and (422) reflexions are given in fig. 4 and in table I.

<table>
<thead>
<tr>
<th>reflex</th>
<th>$1 - \epsilon_H$</th>
<th>average temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>0.0406</td>
<td>23.4 °C</td>
</tr>
<tr>
<td>400</td>
<td>0.0808</td>
<td>23.1 °C</td>
</tr>
<tr>
<td>422</td>
<td>0.1213</td>
<td>24.2 °C</td>
</tr>
</tbody>
</table>

TABLE I
Experimental values of $(1 - \epsilon_H)$ at room temperature
4.2. Determination of $d\epsilon_H/dT$

According to eqs (15) and (16) $d\epsilon_H/dT$ can be obtained from measurements of the integrated intensity as a function of temperature at constant thickness. The diffracted intensity, however, does not only depend on the absolute temperature but is also critically sensitive to the presence of temperature gradients (see the theoretical analysis by Penning and Polder); an experimental verification will be given in a subsequent paper. It is therefore essential to measure the intensity exactly halfway between the two thermocouples, at which location the temperature gradient is zero when the thermocouples are at the same temperature (see eq. (19)). This geometry was always checked by means of X-rays, because at this location the ratio of the integrated transmitted and reflected intensities does not depend on the absolute temperature. Still, the temperature dependence was actually only measured for the transmitted intensity, because this intensity is far less sensitive for small temperature gradients than the reflected intensity (see also fig. 6). The temperature at the centre of the specimen during the measurement was calculated by means of eq. (18)

Fig. 4. $10\log I_B - 10\log I_{\text{reflexion}}$ versus thickness for the (220) reflexion (curve a), for the (400) reflexion (curve b) and for the (422) reflexion (curve c), obtained at 23.4, 23.1 and 24.2°C, respectively.
A typical plot of \( \log I_T \) versus temperature is shown in fig. 5. The experimental results are tabulated in table II.

**TABLE II**

Experimental results of the temperature dependence

<table>
<thead>
<tr>
<th>specimen</th>
<th>reflex</th>
<th>thickness cm</th>
<th>( \alpha ) (see eq. (15))</th>
<th>( \gamma ) (see eq. (15))</th>
</tr>
</thead>
<tbody>
<tr>
<td>OT 7</td>
<td>(220)</td>
<td>1.39.10(^{-1})</td>
<td>5.96.10(^{-3})</td>
<td>1.14.10(^{-5})</td>
</tr>
<tr>
<td>OT 8I</td>
<td>(220)</td>
<td>1.75.10(^{-1})</td>
<td>7.65.10(^{-3})</td>
<td>1.16.10(^{-5})</td>
</tr>
<tr>
<td>OT 8II</td>
<td>(220)</td>
<td>1.75.10(^{-1})</td>
<td>7.67.10(^{-3})</td>
<td>1.16.10(^{-5})</td>
</tr>
<tr>
<td>OT 6</td>
<td>(220)</td>
<td>2.03.10(^{-1})</td>
<td>8.98.10(^{-3})</td>
<td>1.18.10(^{-5})</td>
</tr>
<tr>
<td>OT 10</td>
<td>(400)</td>
<td>6.80.10(^{-2})</td>
<td>5.71.10(^{-3})</td>
<td>1.00.10(^{-5})</td>
</tr>
<tr>
<td>OT 9</td>
<td>(400)</td>
<td>7.35.10(^{-2})</td>
<td>7.01.10(^{-3})</td>
<td>1.14.10(^{-5})</td>
</tr>
</tbody>
</table>

The average value of \( \gamma \) is 1.13.10\(^{-5}\). From eq. (16) one obtains:

\[
\frac{d\varepsilon_{220}}{dT} = -1.11.10^{-4}/^\circ C, \\
\frac{d\varepsilon_{400}}{dT} = -2.22.10^{-4}/^\circ C, \\
\frac{d\varepsilon_{422}}{dT} = -3.33.10^{-4}/^\circ C. 
\]
5. Discussion

5.1. Accuracy

On the basis of the important parameters obtained it is possible to check that the approximations introduced in the derivation of the intensity relations are justified, and that the combined effect of the approximations introduces a negligible error in the final results.

The inaccuracy in the experimental results appears to be quite consistent with the accumulation of the errors indicated.

5.2. $\Sigma H^2$-relationship

With the temperature dependence obtained it is now possible to reduce the values of $(1 - \epsilon_H)$ for the (220), (400) and (422) reflexions to the same temperature $(25 \, ^\circ C)$. The results are summarized in table III.

<table>
<thead>
<tr>
<th>Reflexion</th>
<th>$(1 - \epsilon_H), 25, ^\circ C$</th>
<th>$(1 - \epsilon_H), 25, ^\circ C$</th>
<th>$\Sigma H^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(220)</td>
<td>0.0408</td>
<td>0.00510</td>
<td></td>
</tr>
<tr>
<td>(400)</td>
<td>0.0812</td>
<td>0.00508</td>
<td></td>
</tr>
<tr>
<td>(422)</td>
<td>0.1216</td>
<td>0.00507</td>
<td></td>
</tr>
</tbody>
</table>

The $\Sigma H^2$-relationship is very well obeyed.

Our values of $(1 - \epsilon_H)$ are somewhat smaller than those obtained by Hunter $^5$ (see table IV $^*$). Hunter's values turn out to be slightly smaller if the normal absorption coefficient is taken as 352 cm$^{-1}$ instead of Hunter's value of 326 cm$^{-1}$. Then, too, his results are probably less accurate, because first he uses a slightly inadequate approximation for the integrated intensity, secondly he obtained $\epsilon_{400}$ and $\epsilon_{422}$ from an experiment in which the thickness of the specimen played an important part, and thirdly he did not take the effect of temperature into consideration.

Very recently other data became available, which are also collected in table IV. Our results agree very well with the experimental values obtained by Hildebrandt $^{17}$ and with the value for $(1 - \epsilon_{400})$ obtained by Batterman $^{18}$. Wagenfeld $^{19}$ calculated $\epsilon_H$ on a quantum-mechanical basis. His results, but now corrected for the Debije temperature found experimentally (see next section),

$^*$ We consider Hunter's original results, i.e. those without the strain correction, to be more reliable because, since his interpretation of the effect of strain is not correct, the strain corrections must not be applied $^7$.
are also shown. The agreement between theory and experiment is quite good. Batterman's value for \((1 - \varepsilon_{220})\) differs from the other values by about 40\%; the reason for this discrepancy is not known.

**TABLE IV**

\[(1 - \varepsilon_H)\] obtained by different investigators

<table>
<thead>
<tr>
<th>reflexion</th>
<th>Hunter (^5)</th>
<th>Batterman (^18) - 25 °C</th>
<th>Hildebrandt (^17)</th>
<th>Wagenfeld (^19) - corrected for (\theta_D = 294 ^\circ K)</th>
<th>present work 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>0.047</td>
<td>0.026</td>
<td>0.042</td>
<td>0.046</td>
<td>0.0408</td>
</tr>
<tr>
<td>400</td>
<td>0.10</td>
<td>0.083</td>
<td>0.081</td>
<td>0.088</td>
<td>0.0812</td>
</tr>
<tr>
<td>422</td>
<td>0.15</td>
<td>--</td>
<td>0.117</td>
<td>0.128</td>
<td>0.1216</td>
</tr>
</tbody>
</table>

5.3. *The temperature dependence*

The results in table II show that the temperature coefficient \(\gamma\) is a constant, within the experimental error, thus supporting the discussion in sec. 2. By trial and error, on the basis of eqs (12) and (13), \(\theta_D\) can be calculated. The value of 294 ± 5 °C gives the proper temperature dependence.

It should be pointed out that the anomalously transmitted intensity depends strongly on the temperature, due to the factor \((\frac{1}{2} + \mu_0 l)\), where \(\mu_0 l\) is of the order of 20 to 70. The effect of temperature on the anomalous transmission of Cu Ka radiation in germanium has also been investigated by Batterman \(^19\). He also finds that the integrated reflected intensity decreases exponentially with increasing temperature. However, in his case the decrease in intensity is more rapid than that observed by us.

Batterman initially interpreted his experimental results by assuming that

\[
\varepsilon(T) = \varepsilon_0 \exp \left(\frac{-2\pi^2 n^2}{d^2} u^2\right) = \varepsilon_0 \exp (-M(\theta_D)).
\]

In this way he obtained 254 and 257 °K for the Debye temperature of the (220) and (400) reflexions respectively. These values differ from the value of \(\theta_D = 291 ^\circ K\) he obtained from the temperature dependence of Bragg reflexions \(^20\). Consequently Batterman accepted the value of 291 °K as the correct one and then interpreted his experiments on the basis of

\[
\varepsilon(T) = \varepsilon_0 \exp (-1.32 M(\theta_D)).
\]
Thus the value of the exponent lies somewhere between \(-M(\theta_D)\) and \(-2M(\theta_D)\), the limits for a perfect crystal and an ideally imperfect crystal.

However, it is possible to interpret Batterman's results in quite a different way, without invoking his speculation about the irrational exponent of \(-1.32M(\theta_D)\). We suggest that Batterman's samples were subjected to a temperature gradient during the measurements. From the experiments by Borrmann and Hildebrandt and by Okkerse, and from the theoretical considerations put forward by Penning and Polder, it is known that the temperature gradient perpendicular to the reflecting planes has a marked effect on the diffracted intensities. Now Battermann, in his paper, concluded that part of his (400)-specimen was subjected to a temperature gradient. The qualitative behaviour of the integrated transmitted and reflected intensities in the presence of temperature gradients is illustrated in fig. 6. From Batterman's experimental set-up it follows that if there is a temperature gradient it should be positive, which means that too small a value would be obtained for the integrated reflected intensity. Now we assume that the temperature gradient is proportional to the reduced temperature. One can then show that the integrated reflected intensity still depends exponentially on the absolute temperature, provided that the integrated reflected intensity depends linearly on the temperature gradient. Such an approximation is correct for not too large gradients. This means that Batterman's criterion for the absence of temperature gradients, namely a linear plot of \(\log I_R\) versus \(T\), is not sufficient. It appears that his experimental data can be described in our terms, that is with a Debye temperature of 294 °C, if

\(\ast\) Temperature gradients parallel to the reflecting planes have no effect on the integrated intensities.
it is assumed that at 300 °C his specimens were subjected to a temperature gradient of about 20 °C/cm.

The experimental value for the Debye temperature of $294 \pm 5 \, ^\circ K$ is in good agreement with the value of $291 \, ^\circ K$ obtained by Batterman and Chipman $^{20}$ from the temperature dependence of Bragg reflexions from germanium powder. From heat-capacity measurements by Estermann and Weertman $^{21}$ one obtains by extrapolation a value of about $400 \, ^\circ K$. According to Blackmann $^{22}$ the apparent discrepancy between the values of $\theta_D$ obtained from different phenomena should not be taken too seriously since the relative importance of different parts of the phonon-frequency spectrum may be quite different for X-ray diffraction and the specific heat.

Acknowledgement

The author wants to express his gratitude to his colleagues Dr P. Braun, Ir P. Penning and Prof. D. Polder for the many stimulating discussions during the course of this work. His sincere thanks are also due to Mr A. H. Goemans, who assisted skilfully in the experiments. He wishes to thank Dr G. Hildebrandt and Dr H. Wagenfeld, both from the Fritz Haber Institute, Berlin - Dahlem, for making available their results before publication.

Eindhoven, August 1962

REFERENCES

7) B. Okkerse, Philips Res. Repts, to be published.
15) B. Okkerse, Philips tech. Rev., to be published.
17) G. Hildebrandt, private communication.