Absorption of X-rays in Germanium

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The absorption coefficient of X-rays in germanium was measured for 32 wavelengths in the interval $2\cdot3$ Å $> \lambda > 0\cdot3$ Å ($\lambda_K = 1\cdot12$ Å). A detailed analysis is given, including a comparison with theoretical expressions and a calculation of the oscillator strength for the K-electrons. Agreement between theory and experiment is remarkable. Hydrogen-type wave functions give $g_K = 1\cdot28$ for the dipole oscillator strength. A calculation based on the Thomas–Reiche–Kuhn sum rule and Hartree–Fock type wave functions gives $g_K = 1\cdot29$, while the authors' experimental value is $g_K = 1\cdot27 \pm 0\cdot02$.

Introduction

Absorption coefficients for the elements have in general only been measured for relatively few standard wavelengths (Cu $K\alpha$ etc.). In our work on anomalous transmission of X-rays in germanium (Persson & Grimvall, 1968) for various wavelengths on both sides of the K-absorption edge, we have met a need for more detailed information about the linear absorption coefficient τ. We have therefore measured τ in germanium for 32 different wavelengths in the interval $2\cdot3$ Å $> \lambda > 0\cdot3$ Å ($\lambda_K = 1\cdot12$ Å). With such detailed information about the absorption as a function of wavelength, it is also possible to make a comparison with the theories of anomalous scattering from atoms. Thus we can test to a high degree of accuracy the usual approach with hydrogen-type wave functions for both the bound and free electron states in a photoelectric absorption. The oscillator strength of the K-electrons is also easily obtained and can be compared with theoretical values. If the absorption is known only at a single wavelength one can make a comparison with the theoretical values of the imaginary part of the anomalous contribution to the atomic scattering factor, but not with the real part, nor with the oscillator strength, since these are obtained by integration over a range of wavelengths. It is thus essential to have experimental values of the absorption for many wavelengths.

Experimental technique

The measurements were carried out with an X-ray double-crystal spectrometer, which has been described previously (Brogren, 1951). The X-ray intensities were recorded with a scintillation detector connected to a linear amplifier and a pulse height analyzer. A plane-parallel germanium single crystal with the (220) plane parallel to the surface was used as the monochromator crystal. The crystal under investigation was prepared from a plane-parallel germanium single crystal cut for symmetric Laue reflexion. Its dimensions were $24\cdot8 \times 14\cdot7 \times 0\cdot24$ mm. The surface $24\cdot8 \times 14\cdot7$ was parallel to

the plane (220). The miscutting, *i.e.* the angle between the (422) plane and the surface in the horizontal and vertical directions, was known. The dislocation density was less than 100 cm^{-2}. By chemical etching with iodine etch B (Wang, 1958) a final thickness of about $0\cdot04$ mm was achieved.

During the measurements of the transmitted radiation for every wavelength, the crystal was in a position where the X-ray beam from the monochromator crystal was perpendicular to the $24\cdot8 \times 14\cdot7$ surface. This position was determined as follows: the position at which the (220) planes of the monochromator and analyzer crystal were parallel (the exact position for Bragg–Laue reflexion) was noted from an angular scale. The Bragg angle for the wavelength in question, and the miscutting angle were added to this value, to give the desired position.

The thickness of the analyser crystal was determined in an indirect way. Several authors have reported measurements of the linear absorption coefficient τ for Cu $K\alpha$ radiation ($1\cdot541$ Å). The most accurate values are: 350 cm^{-1} (Hildebrandt & Wagenfeld, 1963), 352 cm^{-1} (Batterman, 1962) and 353 cm^{-1} (Bonse, 1961), giving the mean value $\tau = 352$ cm^{-1}. The spectrometer was adjusted for Cu $K\alpha$ radiation. An area on the crystal was found, where the thickness was constant. The transmitted intensity I was measured for about 10 different positions of the monochromator crystal, *i.e.* for 10 different spots on the analyser crystal within the area of constant thickness. The crystal was then turned to a position parallel to the incident beam and withdrawn from it. The incident beam intensity I_0 was measured for the same positions of the monochromator crystal as above. Knowing τ, the thickness was calculated from the relation $I = I_0 \exp(-\tau t)$. The thickness t was checked regularly during the measurements. The mean value was $t = 43\cdot7 \pm 0\cdot1$ μm.

Using the reference value of $\tau = 352$ cm^{-1}, the linear absorption coefficient was then obtained for other wavelengths as indicated above. It is possible to calculate the position of the monochromator crystal for each wavelength such that the same area of the analyzer

crystal is struck by the incident beam. The 32 wavelengths used were emission lines from Cr, Fe, Cu, W, Mo and Ag targets and wavelengths obtained from the continuous spectrum of a tungsten target. For some of the wavelengths corresponding to emission lines we also made measurements with monochromated radiation from the continuous spectrum of the tungsten target. The spread in the results for a given wavelength was the same as in a remeasurement with the emission line. This confirms the reliability of our use of continuous radiation (except for the region just above the K edge, see the following discussion).

One particular difficulty that arose was the presence of germanium K fluorescent radiation from the monochromator crystal for wavelengths close to the K-absorption edge (1·117 Å). This radiation falls on the long wavelength side of the edge, where the absorption coefficient is low. When wavelengths obtained from the continuous spectrum or emission lines with low intensity are used, the contribution from the fluorescent radiation to the Bragg reflected beam is considerable. The contribution for different experimental conditions has been determined in connexion with the investigations of the anomalous transmission of X-rays in thick germanium crystals (Brogren, Efimov & Persson, 1968). All the results for τ are corrected for the influence of fluorescent X-ray radiation.

There is also another difficulty that will arise when measurements are made very close to the K edge of germanium: the beam which is reflected from the monochromator crystal represents a spectral window, the width of which depends on the widths of the slits that limit the beam. For wavelengths near the K edge, the spectral window was about 0·014 Å for the slit widths used. Details about the determination of this window and its influence on the experimental results will be published elsewhere. Within the wavelength interval 1·117 ± 0·007 Å the role of the finite window must be considered. This is not necessary in the present investigation, where the wavelengths nearest to the K edge are 1·099 Å and 1·125 Å. Measurements of τ for wavelengths near the K edge will be made later with a triple-crystal spectrometer. The spectral window is then very small, so its influence is negligible. Another advantage is that the fluorescent radiation will be much weaker.

Theory

We shall give a brief summary of some well known relationships of which details can be found elsewhere. (James, 1962, Bethe & Salpeter, 1957). The total atomic scattering factor f is in general complex. It is given by

$$f = f_0 + \Delta f' + i\Delta f'' \tag{1}$$

where f_0 is the atomic scattering factor neglecting anomalous scattering, i.e. valid at frequencies much higher than any absorption edge. The anomalous contribution is given by the real and imaginary quantities $\Delta f'$ and $i\Delta f''$. Let $(dg/d\omega)_j$ be the oscillator density of

electron j at frequency ω, ω_j the frequency of the absorption edge j, and ω_i the frequency of the incident X-ray beam. Then

$$\Delta f' = \sum_j \int_{\omega_j}^{\infty} \frac{\omega^2 (dg/d\omega)_j d\omega}{\omega_i^2 - \omega^2} \tag{2}$$

$$\Delta f'' = \frac{\pi \omega_i}{2} \sum_j (dg/d\omega)_j . \tag{3}$$

The total oscillator strength g_j for photoelectric absorption is given by

$$g_j = \int_{\omega_j}^{\infty} (dg/d\omega)_j d\omega . \tag{4}$$

The atomic photoelectric absorption coefficient $\mu(\omega)$ can be expressed in $dg/d\omega$ as

$$\mu(\omega) = \frac{2\pi^2 e^2}{mc} (dg/d\omega) . \tag{5}$$

The linear absorption coefficient τ is related to μ by

$$\tau = N\mu \tag{6}$$

where N is the number of atoms per unit volume. Thus by measuring the linear absorption coefficient τ, the contribution $i\Delta f''$ to the anomalous scattering is immediately obtained. By integration it is also possible to obtain the real part $\Delta f'$ as well as the oscillator strength g_j (equations 2 and 4).

It is customary to express the absorption coefficient μ as a simple function of the wavelength,

$$\mu(\lambda) = \sum C_n \lambda^n \tag{7}$$

where the values of n are in general not integers. It often turns out to be a very good approximation when only one term is kept in the sum (7). Equation (4) is then easily integrated to give

$$g_j = \frac{mc^2}{\pi e^2 \lambda_j (n-1)} \mu(\lambda_j) . \tag{8}$$

Equation (2) is more difficult to handle. Parratt & Hempstead (1954) have solved it for $n = 2$, 7/3, 5/2, 11/4, 3 and 4. The extension to several terms in the sum (7) is trivial.

In the literature there are rather few theoretical calculations of the absorption coefficient (or the equivalent, $dg/d\omega$). Generally, first principles calculations are based on hydrogen-type wave functions for both the bound and free electron states in a photoelectric absorption process (Hönl, 1933, Eisenlohr & Müller, 1954, Wagenfeld, 1966, Guttmann & Wagenfeld, 1967). The electron–electron interaction is taken into account by the use of screening constants and an additional constant potential from the electrons outside the considered shell. For the K-shell $(dg/d\omega)_K$ then has a very simple form (taking only the dipole contribution into account and thus neglecting quadrupole and higher

corrections):

$$(dg/d\omega)_K = \frac{2^8 e^{-4}}{9\omega_K} \left\{ \frac{4}{(1-\delta_K)^2} \left(\frac{\omega_K}{\omega}\right)^3 \right.$$
$$\left. - \frac{1}{(1-\delta_K)^3} \left(\frac{\omega_K}{\omega}\right)^4 \right\}. \quad (9)$$

Here δ_K is a constant characteristic for each element (Hönl, 1933). This expression, given by Hönl (1933), is a very good approximation to a slightly different form used by Wagenfeld (1966). See the Appendix for details. We note that Hönl's form corresponds to two terms in the sum, with $n=3$ and $n=4$. The corresponding expressions for the contributions from L- and M-electrons are much more complicated. A numerical evaluation of these terms (including the quadrupole contribution) has been done by Guttman & Wagenfeld (1967). We recall that the approach was based on matrix elements between bound and free electron states using hydrogen-type wave functions. It can thus be rather unreliable for the contributions from the outer electron shells. The total oscillator strength g is much better obtained from the Thomas–Reiche–Kuhn sum rule (see James, 1962 or Bethe & Salpeter, 1957):

$$\sum_{n \text{ unocc.}} g(j,n) = 1 \quad (10)$$

where n covers all unoccupied states, including the continuum. Therefore, for the K-electrons

$$g_K = 2[1 - \sum_{m \text{ occ.}} g(K,m)] \quad (11)$$

where m now covers all occupied states. $g(j,n)$ is the oscillator strength for transition from state j to state n. We should point out that the sum rule only holds for the 'dipole' term of the oscillator strength, i.e. with neglect of retardation effects. In the last sum, (11), we have matrix elements between two low lying bound states. The corresponding wave functions are known to a high degree of accuracy from numerical calculations of the Hartree–Fock type, so this sum can be accurately determined.

In a calculation where an accuracy of the order of one per cent is wanted, there are several points that require a closer investigation. First, the attenuation of an X-ray beam is not altogether a pure photoelectric effect even in a perfect crystal. The photon can also be scattered without being annihilated. The absorption coefficient τ_{KN} for these processes is generally calculated from the Klein–Nishina formula (Bethe & Salpeter, 1957) for scattering by free electrons. The absorption is practically constant ($\tau_{KN} \sim 1$ cm^{-1}) for all wavelengths of interest to us. It is only for short wavelengths ($\lambda \lesssim \lambda_K/3$) that this correction is of any importance, but, on the other hand the Klein–Nishina formula holds better the shorter the wavelength.

In the discussion on the Thomas–Reiche–Kuhn sum rule, it was stated that it holds only in the 'dipole' approximation. This means that the wavelength of the incoming photon should be large compared to the dimensions of the electron shell considered. This is definitely not true for short wavelengths, but estimates of the higher terms (quadrupole, octupole and dipole-octupole) can easily be made (see Appendix for details). The total contribution to the attenuation from these higher terms is small for all elements when $\lambda \gtrsim \lambda_K/2$. See Fig. 5. Finally, we should mention that many body effects can arise in the atomic absorption. These are, however, expected to be unimportant in the X-ray region (Brandt & Lundqvist, 1965). In our analysis we assume all other effects (deviation from the free atom case due to the crystal lattice etc.) to be negligible.

Results

In Fig. 1 we give $\log \tau$ as a function of $\log \lambda$. τ is expressed in cm^{-1} and λ in Å. Crosses denote points from the use of emission lines and circles points obtained with the continuous tungsten spectrum. Experimental values from other authors (Batterman, 1962, Bonse, 1961, Hildebrandt & Wagenfeld, 1963) are also given. The dashed line is the theoretical calculation by Wagenfeld mentioned in the previous section. The overall agreement between theory and experiment is remarkably good in view of the approximations made in the theoretical approach. Even at longer wavelengths ($\lambda > \lambda_K$) the relative difference is not as large as might be expected since the assumptions in the theoretical calculation are certainly crude for the outer electrons.

One of our main interests will be a thorough discussion of the K-electrons. It is therefore essential to subtract properly, from the value of τ measured for $\lambda < \lambda_K$, a contribution from the L- and M-electrons. We have fitted all experimental points for $\lambda \geq 1.24$ Å (i.e. all those measured with emission lines) to an expression of the form $\tau = C\lambda^n$ by means of a 'least squares' procedure. We obtained $C = 103$ and $n = 2.85$ with τ in cm^{-1} and λ in Å. The difference $(\tau_{\exp} - \tau_{\text{fit}})/\tau_{\exp}$ is shown in Fig. 2. We see that for $\lambda \geq 1.24$ there is no need for a more complicated form of τ than $\tau = C\lambda^n$. This function was then extrapolated to below the K-edge to obtain an absorption τ_K not including the contributions from the L- and M-electrons. Thus we did not take into account the measured values for $\lambda_K < \lambda < 1.24$ Å. There are several reasons for this: fitting the points to this part would appreciably change the extrapolated value below the K-edge and, as the experimental accuracy is lower here because of fluorescence, we cannot exclude the possibility that the small (2–4%) deviation is spurious.* On the other hand, if there really is some such feature in the total absorption close to the K-edge, there is still every reason to believe that the absorption due to the L- and M-electrons has essentially the same wavelength dependence on either side of it. In this and subsequent fittings, the Klein–

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* Accurate measurements near the K-edge using a triple crystal spectrometer are in progress.

Nishina formula was used to subtract the effect of photon scattering. Thus we arrive at a set of absorption coefficients $\tau_{K,\mathrm{ph}}$ for $\lambda < \lambda_K$, which we assume to be due to pure photoelectric absorption. A fit of $\tau_{K,\mathrm{ph}}$ to a function $\tau_{K,\mathrm{ph}} = C_K \lambda^{n_K}$ gives $C_K = 749$ cm^{-1} and $n_K = 2\cdot84$ if λ is in Ångstrom units. In Fig.3 we plot

$$[(\tau_{K,\mathrm{ph}})_{\mathrm{fit}} - (\tau_{K,\mathrm{ph}})_{\mathrm{exp}}]/(\tau_{K,\mathrm{ph}})_{\mathrm{exp}} \, .$$

We see that the fit is good for all wavelengths, and that the experimental uncertainty does not allow a more detailed fit. The corresponding relation

$$[(\tau_{K,\mathrm{ph}})_{\mathrm{H\ddot{o}nl}} - (\tau_{K,\mathrm{ph}})_{\mathrm{exp}}]/(\tau_{K,\mathrm{ph}})_{\mathrm{exp}} \, ,$$

with $(\tau_{K,\mathrm{ph}})_{\mathrm{H\ddot{o}nl}}$ from equation (9) and $\delta_K = 0\cdot197$, is shown in Fig.4. It is clear that the equation $\tau = C\lambda^n$ is as good as Hönl's expression and this still holds if we correct the measured values, according to the Appendix, to take into account that Hönl's equation (9) only gives the dipole term.

It is now possible to calculate the anomalous contributions, $\Delta f'$ and $i\Delta f''$, to the atomic scattering factor from the K-electrons. The imaginary part $i\Delta f''$ is immediately obtained from equation (3). The real part

is more difficult to calculate accurately because of the singularity in the integrand of equation (2). As it happens, one term of the form $\tau = C\lambda^n$ is sufficient, so we can use an interpolation between Parratt & Hempstead's (1954) analytic expressions. In Table 1 we give $\Delta f'_K$ and $\Delta f''_K$ for some commonly used wavelengths. For comparison we have also calculated $\Delta f'_K$ and $\Delta f''_K$ from equation (9) with $\delta_K = 0\cdot197$. A more
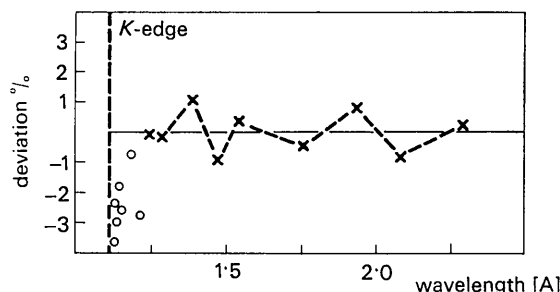
Fig.2. $(\tau_{\mathrm{exp}} - \tau_{\mathrm{fit}})/\tau_{\mathrm{exp}}$ for $\lambda > \lambda_K$. Crosses denote emission lines and circles wavelengths obtained from the continuous tungsten spectrum.
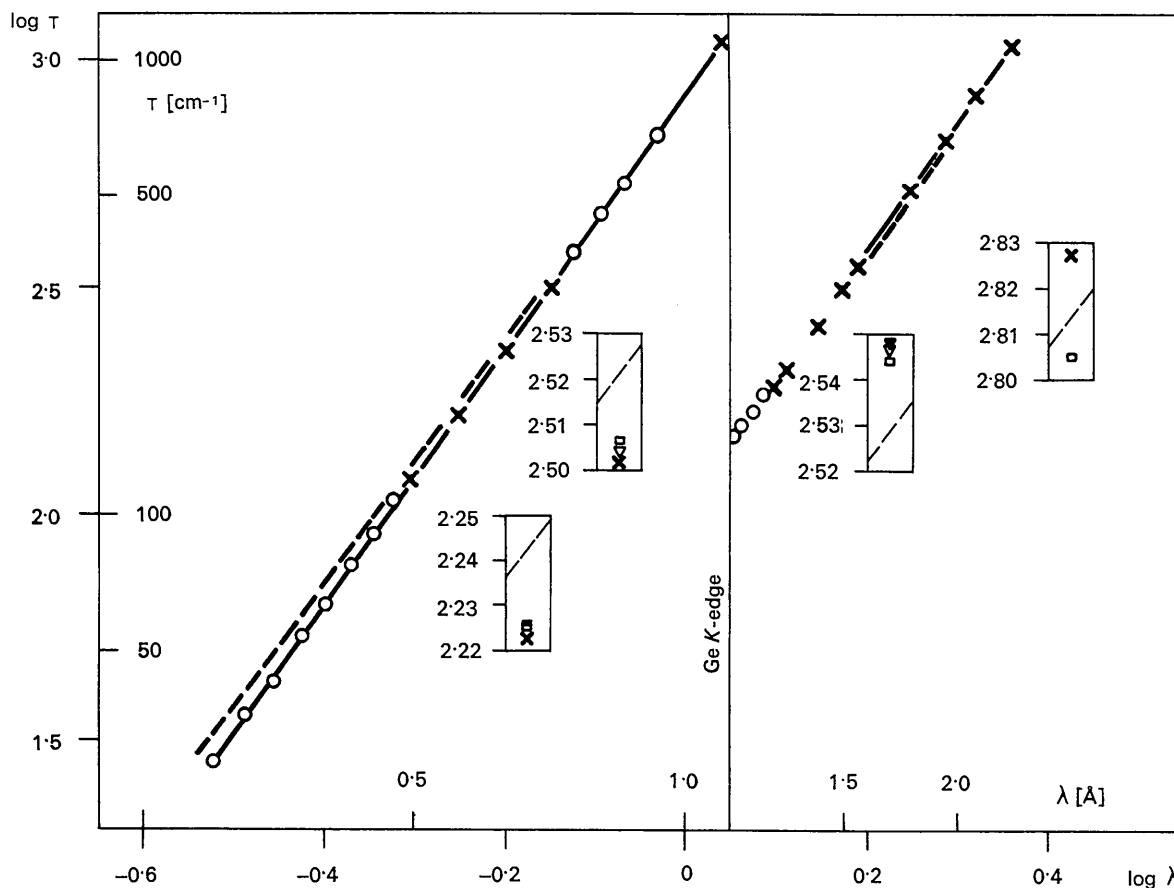
Fig.1. Experimental results for the linear absorption coefficient. τ is expressed in cm^{-1} and λ in Å. Crosses denote emission lines and circles wavelengths obtained from the continuous tungsten spectrum. Dashed line is the theoretical calculation by Guttmann & Wagenfeld. Also shown are experimental values from Batterman ($\triangledown$), Bonse ($\blacktriangledown$), Hildebrandt ($\square$) and Ling & Wagenfeld($\blacksquare$).

detailed comparison between experiment and $\Delta f''_K$ according to the same form of $(dg/d\omega)$, equation (9), was essentially made in Fig. 4. The values of the linear absorption coefficient as determined in our experiments can easily be obtained for any wavelength from the expression for $\tau_{L,M,\mathrm{ph}} = 103\lambda^{2\cdot85}$ cm^{-1}, $\tau_{K,\mathrm{ph}} = 749\lambda^{2\cdot84}$ cm^{-1} and $\tau_{K,N}$ from Bethe & Salpeter (1957). More accurate values can then be obtained with the help of Figs. 2 and 3.

Table 1. *Experimental and theoretical values of the anomalous parts of the scattering factor*

	$\Delta f'_K$		$\Delta f''_K$	
	Experi-		Experi-	
Emission line	ment	Hönl	ment	Hönl
Cu $K\alpha_1$ (1·54 Å)	−1·79	−1·79	—	—
Mo $K\alpha_1$ (0·71 Å)	0·08	0·04	1·58	1·65
Ag $K\alpha_1$ (0·56 Å)	0·27	0·26	1·06	1·07

The oscillator strength g_K can easily be obtained from equation (8) and with the fit $\tau = C\lambda^n$. We find $g_K = 1\cdot28$. Before we proceed to a comparison with theory we should make some small corrections to this value. In the region $\lambda < 0\cdot3$ Å we have no experimental information and keep the form $\tau = C\lambda^n$ as determined above. This region contributes only about 10% to the total value of g_K. For $\lambda_K > \lambda > 0\cdot3$ Å we correct for the small difference between experiment and fit (cf. Fig. 3), and also subtract the contributions from the terms higher than the 'dipole' type according to the estimation in the Appendix. Finally we get a 'dipole' oscillator strength $(g_K)_{\mathrm{dip}} = 1\cdot27 \pm 0\cdot02$ to be compared with

Fig. 3. $[(\tau_{K,\mathrm{ph}})_{\mathrm{fit}} - (\tau_{K,\mathrm{ph}})_{\mathrm{exp}}]/(\tau_{K,\mathrm{ph}})_{\mathrm{exp}}$. $\tau_{K,\mathrm{ph}}$ is the linear photoelectric absorption coefficient for the K-electrons.

Fig. 4. $[(\tau_{K,\mathrm{ph}})_{\mathrm{Hönl}} - (\tau_{K,\mathrm{ph}})_{\mathrm{exp}}]/(\tau_{K,\mathrm{ph}})_{\mathrm{exp}}$. $(\tau_{K,\mathrm{ph}})_{\mathrm{Hönl}}$ is Hönl's theoretical expression.

the sum rule and Hönl's theoretical expression. The error given for g_K is rather arbitrary, and should be considered as our estimate of the uncertainty in the experiments and their evaluation. In Table 2 we compare our value of $(g_K)_{\mathrm{dip}}$, obtained from experiments, with Cromer's (1965) value from Hartree–Fock type calculations and the Thomas–Reiche–Kuhn sum rule [equation (11)]. We also give $(g_K)_{\mathrm{dip}}$ from Hönl's expression [equation (9) and $\delta_K = 0\cdot197$)].

Table 2. *Experimental and theoretical values of the dipole part of the K oscillator strength*

			Theory, sum
		Theory	rule
	This work	(Hönl, 1933)	(Cromer, 1965)
$(g_K)_{\mathrm{dip}}$	1·27±0·02	1·28	1·29

Conclusions

From Fig. 4 it is evident that the relatively simple expression given by Hönl (cf. Appendix and equation 9) for $\Delta f'$ and $\Delta f''$ gives a very good agreement with experiment. It is natural that $\Delta f''$ shows larger deviations than the real part $\Delta f'$, which contains an average over all wavelengths $\lambda < \lambda_K$. Hönl's expression is especially favourable, as it permits an analytical solution of equation (2) for $\Delta f'$. When it comes to the oscillator strength, both Hönl's expression and the use of the Thomas–Reiche–Kuhn sum rule give values in agreement with experiment. From Cromer's (1965) calculations one finds that Hönl's g_K agrees with the sum rule values to within a few per cent for all the not too heavy elements.

To our knowledge, this is the first time that measurements have been made extensive enough to allow for a detailed comparison with various theoretical approaches. Hönl's theory has been used for a long time, and has, for good reason, been thought to give an adequate description of the anomalous scattering from the K-electrons. It is, of course, very satisfying to find that the agreement between theory and experiment is remarkably good.

APPENDIX

In Wagenfeld's (1966) paper on the numerical evaluation of photoelectric absorption cross sections, he gives the following formulae for the K-shell:

$$\mu_K^D = \frac{2^8 \pi e^2}{3mc^2} \lambda \left(\frac{\lambda}{\lambda_1}\right)^3 \frac{e^{-4n_1' \mathrm{arc\,cot}\, n_1'}}{1 - e^{-2\pi n_1'}} \quad (A1)$$

$$\mu_K^Q = \frac{2\mu_K^D}{5} \frac{\lambda_c}{\lambda} [4 - 3\lambda/\lambda_1] \quad (A2)$$

$$\mu_K^Q = \frac{\mu_K^D}{350} \left(\frac{\lambda_c}{\lambda}\right)^2 [59 - 366\lambda/\lambda_1 + 296(\lambda/\lambda_1)^2] \quad (A3)$$

or

$$\mu_K^Q = \frac{8\mu_K^D}{175} \left(\frac{\lambda_c}{\lambda}\right)^2 [4 - 3\lambda/\lambda_1][9 - 8\lambda/\lambda_1] \quad (A4)$$
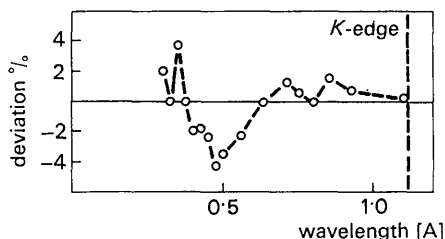
$$\mu_K^{D,O} = \frac{2\mu_K^D}{5} \left(\frac{\lambda_c}{\lambda}\right) [1 - 2\lambda/\lambda_1] \qquad (A5)$$

where D means dipole, O octupole and D,O mixed dipole-octupole. The two terms for μ_K^O correspond to the two different possible final states (angular momentum $l=1$ or $l=3$). λ_1 is defined by $\lambda_1 = [(Z-s)^2R]^{-1}$ where R is the Rydberg constant and s is a screening constant. Further $n' = [\lambda/(\lambda_1-\lambda)]^{1/2}$. For references on the steps leading to equations $(A1)$–$(A5)$ see Wagenfeld's paper. Hönl (1933) has made essentially the same analysis. However, he uses the fact that for $1 \lesssim z \lesssim 4$, it is a good approximation (better than 1·5%) to replace the last factors in equation $(A1)$ by a series expansion, using that

$$e^{-\frac{4}{\sqrt{z-1}}\, arc\, tg\sqrt{z-1}} \Big/ 1 - e^{\frac{-2\pi}{\sqrt{z-1}}} \simeq e^{-4}(4z-1)/3\,. \qquad (A6)$$

Also, Hönl introduces a quantity

$$\delta_K = 1 - (hc/\lambda_K)/E_{K,\,Som}$$

where $E_{K,\,Som}$ is the energy eigenvalue of the K-electrons using Sommerfeld's fine structure formula. Hönl then arrives at the expression of equation (9). If we neglect the fine structure terms we have $\delta_K = 1-\lambda_1/\lambda_K$ and there is agreement between Hönl's and Wagenfeld's expressions except for the series expansion mentioned. For germanium, we have calculated $\delta_K = 0.197$.

From equations $(A1)$–$(A5)$ it is easy to estimate the relative importance of terms higher than the dipole type. Fig. 5 gives results for germanium in the range of wavelengths of interest to us.

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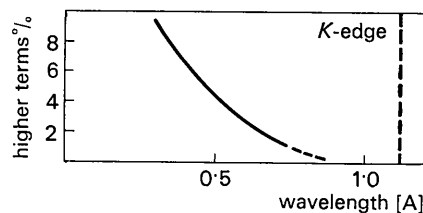

Fig. 5. Relative contribution to the absorption by the K-electrons from terms higher than the dipole type.

body effects in atoms. Grants from Atomforskningsrådet (G.G.) and Naturvetenskapliga forskningsrådet (E.P.) are gratefully acknowledged.

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The Twinning in 1-p-Nitrobenzeneazo-2-naphthol (Para Red)

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Crystals of Para Red have been studied by photographic X-ray methods. Cooling the crystals produced reversible splitting of the diffraction spots. This was traced to the use of crystals twinned by pseudomerohedry, in association with anisotropic thermal contraction. At room temperature the twin obliquity was only $0°22'$ and the diffraction spots of the two twin individuals were not resolved.

Introduction

In the course of an X-ray study of 1-p-nitrobenzeneazo-2-naphthol, a red paint pigment commonly known as

Para Red, some intriguing phenomena were observed when the crystals were cooled. At first these were attributed to some type of phase transformation, and it was not until the structure at room temperature failed