Acta Cryst. (1979). A**35**, 852–857

X-ray Anomalous Scattering Factors for Silicon and Germanium

By L. Gerward and G. Thuesen

Laboratory of Applied Physics III, *Technical University of Denmark, DK*-2800 *Lyngby, Denmark*

M. Stibius Jensen

DIA-B, Technical University of Denmark, DK-2800 *Lyngby, Denmark*

and I. Alstrup

Haldor Topsøe Research Laboratories, DK-2800 *Lyngby, Denmark*

(*Received* 17 *April* 1979; *accepted* 21 *May* 1979)

Abstract

Accurate measurements of X-ray attenuation coefficients for Si and Ge have been used to determine those dispersion corrections which are related to the photoeffect cross section. The results are compared with calculations based on relativistic as well as non-relativistic quantum mechanics. A new notation is proposed to facilitate the comparison between experimental and theoretical results.

1. Introduction

Owing to the need in X-ray crystallography for accurate values of X-ray dispersion corrections and mass absorption coefficients many theoretical estimates of these parameters have been attempted for a large number of elements and for energy ranges corresponding to common X-ray sources. The most recent and most sophisticated calculations are the ones by Cromer & Liberman (1970) (hereafter CL) using relativistic quantum mechanics.

In this paper we report accurate measurements of the total X-ray attenuation coefficients for Si and Ge over a wide range of energies. Contributions due to Compton scattering and thermal diffuse scattering have been calculated and subtracted to give the photoelectric absorption coefficient from which the dispersion corrections can be calculated according to conventional non-relativistic theory. The values thus obtained are compared with the values calculated by CL. Good agreement is found for the imaginary part, f''. However, the values for the real part, f', obtained from the experimental results are systematically larger than the f' values calculated by CL. Several authors, including CL, have made a similar comparison between f' values derived from experimental photoelectric absorption coefficients and CL's theoretical estimates of f'.

An examination of the relativistic theory of the atomic scattering factor f makes it clear, however, that the Kronig expression, which in the conventional non-relativistic theory connects f' and f'', does not apply when the dispersion correction is defined as $f-f_0$, as done by CL, f_0 being the Thomson scattering factor. We therefore propose a new notation for the dispersion corrections. The examination also reveals that at high energies and for high atomic number elements there is a frequency-dependent term in addition to the total energy term used by CL.

2. Non-relativistic theory

In non-relativistic theory the atomic scattering factor f is written as (*e.g.* James, 1969)

$$f=f_0+f'+if'', \tag{1}$$

where the Thomson scattering factor f_0 is given by

$$f_0=\mathbf{e}_2.\mathbf{e}_1\sum_j\langle j|\exp[-i(\mathbf{k}_2-\mathbf{k}_1).\mathbf{r}]|j\rangle. \tag{2}$$

The summation j goes over all occupied orbitals; $\mathbf{e}_1$ and $\mathbf{e}_2$ are the polarization vectors and $\mathbf{k}_1$ and $\mathbf{k}_2$ the wave vectors of the incident and scattered radiation. The dispersion corrections f' and f'' are given by

$$\begin{aligned}f'&+if''\\&=-\frac{1}{m}\sum_j\sum_n\left[\frac{\langle j|\mathbf{e}_2.\mathbf{p}\,e^{-i\mathbf{k}_2.\mathbf{r}}|n\rangle\langle n|\mathbf{e}_1.\mathbf{p}\,e^{i\mathbf{k}_1.\mathbf{r}}|j\rangle}{E_n-E_j-\hbar\omega-i\alpha}\right.\\&\qquad\left.+\frac{\langle j|\mathbf{e}_1.\mathbf{p}\,e^{i\mathbf{k}_1.\mathbf{r}}|n\rangle\langle n|\mathbf{e}_2.\mathbf{p}\,e^{-i\mathbf{k}_2.\mathbf{r}}|j\rangle}{E_n-E_j+\hbar\omega-i\alpha}\right],\end{aligned} \tag{3}$$

where $\mathbf{p}$ is the momentum operator and m the electron mass. The summation n goes over all unoccupied orbitals, including the continuum. α is a positive

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infinitesimal which ensures that the interaction vanishes for $t \to \pm\infty$.

We specialize from now on in the purely forward scattering, *i.e.* $\mathbf{e}_1 = \mathbf{e}_2 = \mathbf{e}$ and $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}$, and obtain for f',

$$f' = -\frac{1}{m} P \sum_j \sum_n \left[\frac{|\langle n|\mathbf{e}.\mathbf{p}\, e^{i\mathbf{k}.\mathbf{r}}|j\rangle|^2}{E_n - E_j - \hbar\omega} + \frac{|\langle n|\mathbf{e}.\mathbf{p}\, e^{-i\mathbf{k}.\mathbf{r}}|j\rangle|^2}{E_n - E_j + \hbar\omega} \right], \tag{4}$$

where P means principal part of the summation in the sense that all terms with zero denominator should be left out. In this case we obtain for f''

$$f'' = -\frac{\pi}{m} \sum_j \sum_n \delta(E_n - E_j - \hbar\omega) |\langle n|\mathbf{e}.\mathbf{p}\, e^{i\mathbf{k}.\mathbf{r}}|j\rangle|^2. \tag{5}$$

We can express f' by means of f'' by rewriting f' in the following way

$$f' = -\frac{1}{m} \int \mathrm{d}\omega'\, P \sum_j \sum_n \delta(\omega_n - \omega_j - \omega') \times \frac{2\omega'}{\hbar} \frac{|\langle n|\mathbf{e}.\mathbf{p}\, e^{i\mathbf{k}.\mathbf{r}}|j\rangle|^2}{\omega'^2 - \omega^2};$$

$$f' = -\frac{2}{m} P \int \mathrm{d}\omega' \left[\sum_j \sum_n \delta(E_n - E_j - \hbar\omega') \times |\langle n|\mathbf{e}.\mathbf{p}\, e^{i\mathbf{k}.\mathbf{r}}|j\rangle|^2 \right] \frac{\omega'}{\omega'^2 - \omega^2};$$

$$f' = \frac{2}{\pi} P \int \mathrm{d}\omega' \frac{\omega' f''(\omega')}{\omega'^2 - \omega^2}. \tag{6}$$

Expression (6) is valid to second order in non-relativistic perturbation theory.

f'' is directly related to the photoelectric cross section, σ_{pe},

$$f'' = -(\omega/4\pi r_e c)\, \sigma_{\mathrm{pe}}, \tag{7}$$

where r_e is the classical electron radius. The negative sign of f'' comes from the use of the time factor $\exp(-i\omega t)$ in the wave equation.

3. Relativistic theory

As stated by CL and in references given by them, expressions similar to the ones given above apply when relativistic theory is used. In this case, however, we get contributions from summation over negative as well as positive intermediate energy states.

CL split f in a similar way as in (1):

$$f = f_0 + f^+ - f_0^+ + (f^- - f_0^-), \tag{8}$$

where f_0 is given by (2). Superscripts + and − correspond to summation over positive and negative energy states, respectively.

The real and imaginary parts, f_r^+ and f_i^+, of f^+ are related through an expression similar to (6);

$$f_r^+ = \frac{2}{\pi} P \int \mathrm{d}\omega' \frac{\omega' f_i^+(\omega')}{\omega'^2 - \omega^2}. \tag{9}$$

The imaginary part of f^+ is related to the photoeffect cross section in the same way as f'' in (7):

$$f_i^+ = -(\omega/4\pi r_e c)\, \sigma_{\mathrm{pe}}. \tag{10}$$

In non-relativistic theory the frequency independent part of f is equal to the Thomson term f_0, which for forward scattering is equal to Z, the number of electrons in the atom. In the relativistic theory an extra term has to be added. CL have evaluated this term in the dipole approximation to be

$$-f_0^+ + (f^- - f_0^-) = 5E_{\mathrm{tot}}/3mc^2, \tag{11}$$

where E_{tot} is the total energy of the atom. The right-hand side of (11) has a constant and negative value for a given element. As will be discussed elsewhere (Stibius Jensen, 1979), this approximation is too crude, however, at high energies and/or for high atomic number elements. It is necessary to add a frequency dependent, magnetic term

$$-\tfrac{1}{2}Z(\hbar\omega/mc^2)^2. \tag{12}$$

4. Experimental procedure

It follows from (6), (7), (9) and (10) that f', f'' of the non-relativistic theory or f^+ of the relativistic theory can be derived from measurements of the photoeffect cross section. The evaluation of the integral for the real part requires that the photoeffect cross section is known in as large an energy range as possible. In this work we have used the experimental linear attenuation coefficients for Si and Ge single crystals given by Gerward & Thuesen (1977), Hildebrandt, Stephenson & Wagenfeld (1973) and Persson & Efimov (1970) in the energy range 5–50 keV. The contributions due to Compton scattering and thermal diffuse scattering have been calculated according to Gerward & Thuesen (1977) and subtracted from the experimental values to give the values of the linear photoelectric absorption coefficient, τ.

For Si we have no experimental values below the K edge and between the K edge and 5 keV. Therefore, theoretical values from Storm & Israel (1970) have been included. It was shown previously that the calculations of Storm & Israel (1970) are in good agreement with our data within the measured energy range. For Ge the fitting could be performed with purely experimental values.

For energies on either side of the K absorption edge the τ values have been fitted by least squares to the expression

$$\tau(\omega) = \sum_{n=2}^{4\,\mathrm{or}\,5} A_n \omega^{-n}, \qquad (13)$$

where A_n are fitting parameters.

Figs. 1* and 2 show the result of the fitting. It is seen that the combined data used in this work form a consistent set for both Si and Ge, the deviations from the fitted values being less than a few per cent and varying in a rather unsystematic way.

Fig. 1 also shows that the slope d(ln τ)/d(ln E) changes with energy, in particular for Si. This means that an analysis based on a constant slope, a procedure often used, may be insufficient. In our case the changing slope made it necessary to include the theoretical Si data between the K edge and 5 keV.

The frequency dependence of the imaginary part of the dispersion correction has been obtained by substituting (13) into (7) or (10) and using $\sigma_{\mathrm{pe}} = \tau/N$, where N is the number of atoms per unit volume. It can be shown that the right-hand side of (6) and (9), describing the real part, can be solved by elementary integrals when inserting the analytic approximation (13).

5. Results

5.1. *Silicon*

The results for Si are summarized in Table 1. Fig. 3(a) shows the real part of the dispersion correction as a function of the energy. The broken line is obtained when the total energy term used by CL, (11) in the present work, is added. One notices that the f' values become negative for large energies when including an energy term of constant and negative value.

Table 1 shows that there is good agreement between the experimental and theoretical values for the imaginary part f'' and the photoelectric mass absorption coefficient τ/ρ. This is true whether the wave-functions are the non-relativistic hydrogen-like ones used by Hildebrandt, Stephenson & Wagenfeld (1973), or the relativistic ones used by CL.

Concerning the real part it follows from (9) that the experimental f' based on the photoelectric absorption should be compared with CL's calculated values of f_r^+ and not with their calculated values of f'. Indeed, when this is done the agreement is excellent as seen in Table

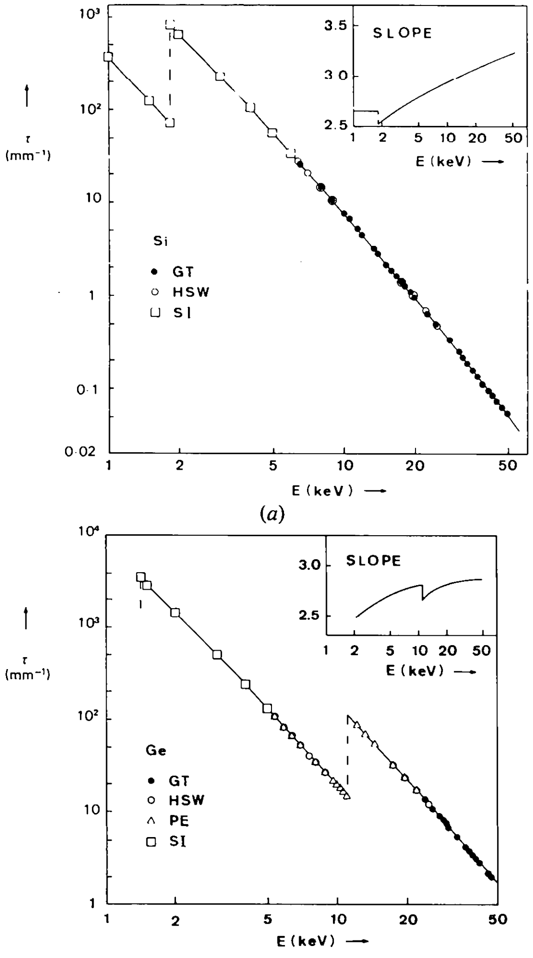

Fig. 1. Photoelectric cross sections. The full line shows the fit according to (6). The enclosure shows the slope $-$d(ln τ)/d(ln E). Filled circles denote values of Gerward & Thuesen (1977), open circles Hildebrandt, Stephenson & Wagenfeld (1973), open triangles Persson & Efimov (1970) and open squares Storm & Israel (1970). (a) Silicon; (b) germanium.

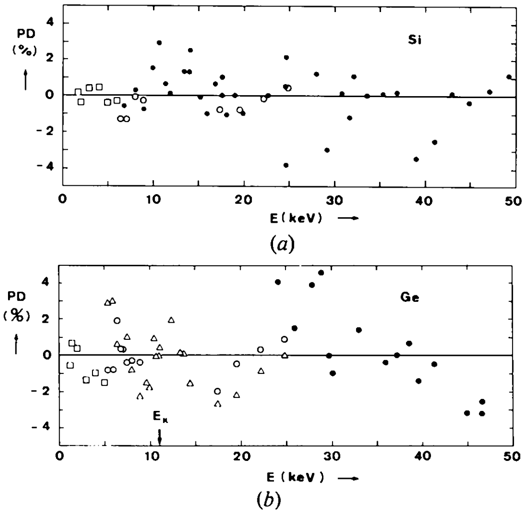

Fig. 2. Percentage difference (PD) between data and fitted values. Symbols as in Fig. 1. (a) Silicon; (b) germanium.

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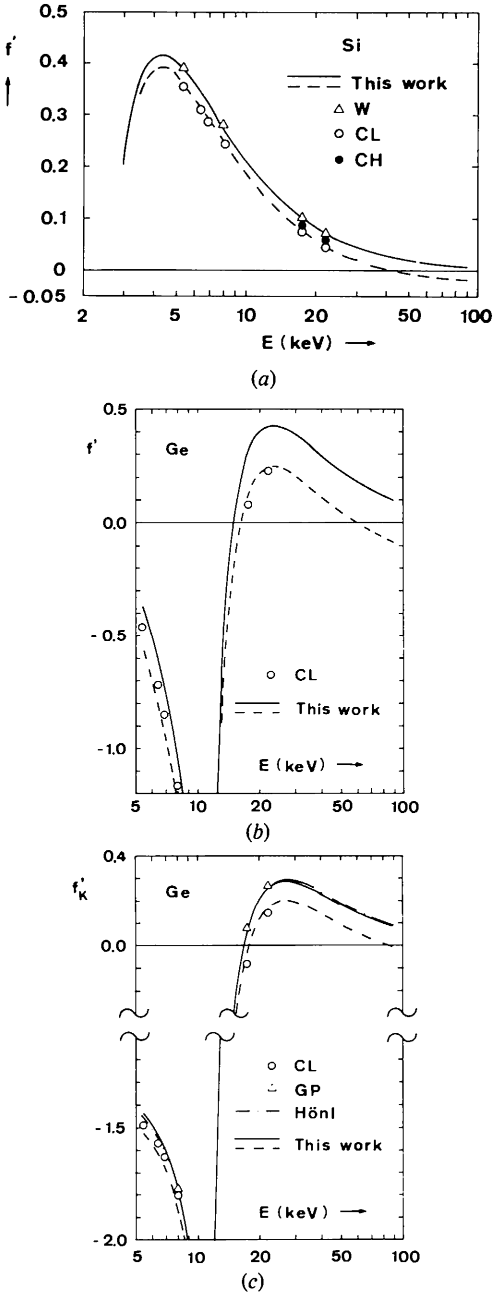
* Note that in this paper SI units have been used for τ(mm^{-1}) and τ/ρ (mm^2/g).

1. The non-relativistic calculations of f' by Wagenfeld (1975) are also in good agreement with the experimental f' values.



(a)

(b)

(c)

Fig. 3. Real part of the dispersion corrections f'. The full line is calculated according to (7); the broken line is obtained by subtracting 0·026 for Si, 0·186 for Ge and 0·088 for Ge K electrons, corresponding to the total energy term in (11); open triangles denote values of (*a*) Wagenfeld (1975), (*c*) Grimvall & Persson (1969), open circles Cromer & Liberman (1970), filled circles Cusatis & Hart (1970). The curve (—·—) has been calculated from Hönl's (1933*a*,*b*) formula. (*a*) Silicon; (*b*) germanium, (*c*) germanium, K electrons only.

5.2. *Germanium*

The results for Ge are similar to those for Si (Fig. 3*b* and Table 2). There is good agreement between the experimental and the theoretical values of f'' and τ/ρ. Good agreement is also found between the experimental values of f' and CL's values for the real part of f^+, in particular for energies above the K edge.

No hydrogen-like calculations for the total f' have been published. However, for Ge it has been possible to extrapolate the analytic approximation (13) for the photoeffect cross section found below the K edge. By subtracting the extrapolated values from the total measured values above the K edge one obtains the contribution due to the K electrons only. The dispersion corrections for the K electrons can now be compared with the hydrogen-like calculation using Hönl's (1933*a*,*b*) formulae (Table 2 and Fig. 3*c*). Once more one finds that the experimental results agree quite well with the hydrogen-like calculations and with the f_K^+ values of CL.

Having the photoeffect cross section due to K electrons only, σ_K, one can calculate the total oscillator strength of the K electrons, g_K (for a definition of g_K see *e.g.* James, 1969) using

$$g_K = (2\pi^2 r_e c)^{-1} \int_{\omega_K}^{\infty} \sigma_K(\omega)\, d\omega. \qquad (14)$$

Table 1. *Summary of results for* Si

The imaginary part, τ/ρ in mm^2/g and $f8'$ (positive values used). The experimental absorption coefficients have been corrected for the scattering contributions.

	This work experimental		CL theoretical		HSW theoretical	
	τ/ρ	f''	τ/ρ	f''	τ/ρ	f''
Cr *Kα*	19270	0·696	19190	0·693	19210	0·694
Fe	11950	0·510	11910	0·509	11880	0·507
Co	9521	0·440	9480	0·438	9450	0·437
Cu	6174	0·331	6150	0·330	6120	0·328
Mo	612	0·071	610	0·071	611	0·071
Ag	295	0·044	290	0·043	297	0·044

The real part, f'

	This work experimental	CL theoretical		W theoretical	CH experimental
		f_r^+	f'		
Cr *Kα*	0·389	0·381	0·355	0·406	
Fe	0·344	0·337	0·311		
Co	0·320	0·313	0·287		
Cu	0·274	0·270	0·244	0·280	
Mo	0·099	0·098	0·072	0·101	0·086
Ag	0·070	0·068	0·042	0·071	0·057

CL = Cromer & Liberman (1970, 1976), relativistic wavefunctions; HSW = Hildebrandt, Stephenson & Wagenfeld (1973), non-relativistic hydrogen-like wavefunctions; W = Wagenfeld (1975), non-relativistic hydrogen-like wavefunctions; CH = Cusatis & Hart (1975), X-ray interferometer.

Table 2. *Summary of results for* Ge

The imaginary part, τ/ρ in mm²/g and f'' (positive values used). The experimental absorption coefficients have been corrected for the scattering contributions.

	This work experimental		CL theoretical		HSW theoretical	
	τ/ρ	f''	τ/ρ	f''	τ/ρ	f''
Cr *Kα*	19850	1·85	19130	1·79	19650	1·83
Fe	12510	1·38	12050	1·33	12130	1·34
Co	10060	1·20	9680	1·16	9660	1·16
Cu	6630	0·92	6390	0·89	6280	0·87
Mo	6100	1·84	5980	1·80	6110	1·84
Ag	3130	1·20	3110	1·19	3200	1·22

The real part, f'

	This work experimental	CL theoretical		f'_K This work	CL		GP	Hönl
		f_r^+	f'		f_r^+	f'		
Cr *Kα*	−0·37	−0·28	−0·46	−1·44	−1·40	−1·49		−1·46
Fe	−0·60	−0·53	−0·72	−1·53	−1·49	−1·57		−1·55
Co	−0·74	−0·66	−0·85	−1·59	−1·54	−1·63		−1·61
Cu	−1·04	−0·98	−1·16	−1·77	−1·72	−1·80	−1·79	−1·79
Mo	0·30	0·27	0·08	0·06	0·01	−0·08	0·08	0·04
Ag	0·43	0·41	0·23	0·26	0·23	0·14	0·27	0·26

Oscillator strength, g_K

	This work exp.	GP exp.	C theor.	Hönl theor.
g_K	1·27	1·27	1·29	1·29

CL = Cromer & Liberman (1970, 1976), relativistic wavefunctions; HSW = Hildebrandt, Stephenson & Wagenfeld (1973), non-relativistic hydrogen-like wavefunctions; GP = Grimvall & Persson (1969), experimental; Hönl (1933*a*,*b*) non-relativistic hydrogen-like wavefunctions; C = Cromer (1965), relativistic wavefunctions.

The integral can be solved analytically using (13) for $\sigma_K(\omega)$. Table 2 shows that the various experimental and theoretical calculations agree within <1%. The result gives some confidence in the extrapolation used for obtaining σ_K.

6. Discussion

As seen above, the f'' values determined from the experimental τ values for Si and Ge are in excellent agreement with the f'' values calculated by CL but systematic deviations are found for f'. Examination of the theory used by CL suggests that these deviations are due to the fact that CL define the dispersion correction, $f' + if''$, as $f - f_0$, where f_0 is the Thomson term. This seems to have created some confusion. Several authors, including CL themselves, make an invalid comparison between the theoretical f' values and the values derived from experimental values of $\sigma_{\rm pe}$ using the Kronig expression (6). Only that part of f, which is related to $\sigma_{\rm pe}$, *viz* f^+, should be compared with the results obtained from photoelectric absorption measurements.

Considering the discussion above we suggest the use of a new notation. Let f' and f'' denote those dispersion corrections which are related to the photoeffect cross section. In the notation of CL they are equal to the real and imaginary parts of f^+. Let $\delta f'$ denote the relativistic correction to $f - f^+$. With the proposed notation the atomic scattering factor is written

$$f = f_0 + f' + \delta f' + if'', \qquad (15)$$

where f' and f'' are given by (6) and (7) or the equivalent (9) and (10), and $\delta f'$ is given by

$$\delta f' \equiv -f_0^+ + (f^- - f_0^-), \qquad (16)$$

using the notation of CL on the right-hand side of (16). According to our considerations $\delta f'$ should be the sum of the contributions (11) and (12).

With these new definitions good agreement has been obtained between experimental and theoretical values of f' and f'' for Si and Ge. However, other types of experiments are necessary for the determination of $\delta f'$. It can only be done by determining the real part of the total scattering factor f with very high accuracy and subtracting f_0 and f'. In principle it can be done by measuring the refractive index for X-rays or by a direct scattering experiment.

Interferometer determination of the real part of f has recently been reported for Si by Cusatis & Hart (1975). The results obtained are shown in Table 1. It is seen that the values are in between those obtained from the photoeffect cross section and CL's f' values. If the CL values are corrected by adding the magnetic term (12), then the difference between Cusatis & Hart's (1975) experimental values and the theoretical values increases. However, further experimental values would be desirable before drawing any definite conclusions from the observed discrepancy.

Tirsell, Slivinsky & Ebert (1975) have made an attempt to determine $|f|$ directly by scattering experiments. They used much higher photon energies so relativistic corrections are expected to be larger than in our case. The intensity of the scattered beam was determined for a number of angles but not for forward scattering. The relativistic theory of the angular dependence of f has not yet been worked out. It is therefore not yet possible to analyze these experiments and to use them as a test of the theory.

7. Conclusion

Values for those dispersion corrections which are related to the photoeffect cross section have been determined from experimental values of the photoelectric absorption coefficients for Si and Ge. The values are in excellent agreement with theoretical ones. Relativistic effects influence these results to a negligible degree in the energy range of the experiments. On the other hand, relativistic calculations show that at high photon energies and/or for high atomic number elements the remaining part of f consists not only of the Thomson term f_0 but an additional term $\delta f'$. The latter term has until now not been determined with sufficient accuracy either theoretically or experimentally.

Note added in proof: The theoretical values calculated by Hildebrandt, Stephenson & Wagenfeld (1973) can only be considered as an approximation for low-Z elements since they use averaged screening constants. Improved calculations have been published by Stephenson (1976) for $Z = 2$ to 23. However, the results for silicon differ very little from those quoted in the present work.

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SHORT COMMUNICATIONS

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Acta Cryst. (1979). A**35**, 857–858

Sign reversal of piezo-optic birefringence in mixed crystals of KCl–KBr.

By G. S. Kumar, R. Ethiraj and V. G. Krishna Murty, *Department of Physics, Osmania University, Hyderabad* 500 007, *India*

(*Received* 15 *December* 1978; *accepted* 18 *April* 1979)

Abstract

The dispersion of stress–optical coefficient C_{001} of mixed crystals of KCl–KBr is measured in the wavelength range 250–520 nm. Sign reversal of C_{001} is observed in all crystals studied.

Recently, Ethiraj, Krishna Murty & Bansigir (1978) have studied the dispersion of piezo-optic birefringence characterized by the stress–optical coefficients C_{001} (stress along a cube axis and observation along another axis) and C_{110} (stress along a face diagonal and observation along a cube axis) in mixed crystals of KCl–KBr in the wavelength range 300–620 nm. They found that the values of these coefficients decrease more rapidly with decrease of wavelength (dispersion larger) than in the case of pure crystals. In earlier studies on piezo-optic dispersion, a reversal in the sign of the coefficients C_{001} and C_{110} has been observed in the ultraviolet region in the case of some alkali halide crystals (KCl, KBr and KI: Srinivasan, 1959; Rahman & Iyengar, 1967; RbBr, RbI, CsCl and CsI: Laiho & Korpela, 1968). In order to see whether the stress–optical coefficients, C_{001}, of mixed crystals of KCl–KBr undergo reversal in sign as in the case of pure crystals, their dispersion was measured in the wavelength range 250–520 nm and the results obtained are reported in this paper.

The experimental method described by Ethiraj, Krishna Murty & Bansigir (1978) was employed for evaluating the coefficient C_{001} at different wavelengths of KCl, KBr and five mixed crystals of KCl–KBr. The crystals grown by Ethiraj, Krishna Murty & Bansigir (1978) were used in the present investigation. The dispersion curves for all the crystals studied are shown in Fig. 1. As can be seen from Fig. 1, the value of C_{001} of each crystal decreases slowly at first and then rapidly with the decrease of wavelength and undergoes a reversal in its sign at a particular wavelength (λ_{rev}) depending on the composition of the crystal. In KCl and KBr, the sign reversal occurs at 251 nm and 273 nm, respectively. These values are in good agreement with the values 255 nm and 276 nm reported by Srinivasan (1959) for these crystals. In Fig. 2 are plotted the reversal wavelengths as a function of mol% of KBr for all crystals. It is interesting to note that the λ_{rev} varies non-linearly with mol% of KBr