$$\frac{Q'}{Q} = 1 - a_1\frac{p_2}{p_1^2}(Q_0p_1) + a_2\frac{p_3}{p_1^3}(Q_0p_1)^2 + \ldots$$

where

symmetrical Laue case

$$a_1 = 2t_0^2 \tan\theta/3\lambda \qquad a_2 = \tfrac{33}{40}a_1^2$$

symmetrical Bragg case

$$a_1 = 2t_0^2 \operatorname{cotan}\theta/3\lambda \qquad a_2 = \tfrac{6}{5}a_1^2\,,$$

$t_0$ being the thickness of a single mosaic block. Thus the primary and secondary extinction corrections are of the same form and it is difficult, if not impossible, to make an experimental distinction.

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# Dispersion in Quartz

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With Cu $K\alpha$ radiation diffraction intensities $I_H$ and $I_{\bar{H}}$ of quartz were found to differ by as much as fifty per cent.

The observations gave a value of $\Delta = 0{\cdot}31 \pm 0{\cdot}01$ for the imaginary dispersion correction of silicon and are in good agreement with theory.

## Introduction

A convenient experimental measure of the dispersion effect in asymmetric crystals is the dimensionless quantity ,$X_H$, defined by

$$X_H = \frac{I_H - I_{\bar{H}}}{\frac{1}{2}(I_H + I_{\bar{H}})} = \frac{|F'_H|^2 - |F'_{\bar{H}}|^2}{\frac{1}{2}(|F'_H|^2 + |F'_{\bar{H}}|^2}\,. \qquad (1)$$

As stated in the preceding paper (Zachariasen & Plettinger, 1965) large deviations from Friedel's rule were found for quartz and Cu $K\alpha$ radiation. Indeed, values of $|X_H|$ up to 0·5 were observed for some reflection pairs. The magnitude of the dispersion effects was greater than anticipated, for the Cu $K\alpha$ wave length is less than one fourth that of the nearest critical absorption edge. Moreover, the recent study of quartz by Smith & Alexander (1963), in which also Cu $K\alpha$ radiation was used, does not report any intensity differences $I_H - I_{\bar{H}}$. For these reasons it seemed desirable to demonstrate that the observed dispersion effects were in agreement with theory.

The formal treatment of dispersion in X-ray diffraction theory is well known and has been given in various text books (see for instance sections III, 4, 5, 9, 12 of Zachariasen, 1945). However, it will be useful to give some of the general theoretical results in detailed form so as to facilitate comparison with experiment.

## Theoretical considerations

The atomic scattering power is of the form $f' = f_0 + \Delta' + i\Delta = f + i\Delta = f(1 + i\delta)$. The imaginary term implies true absorption, the corresponding atomic absorption coefficient, $\mu_a$, being

$$\mu_a = \frac{2e^2\lambda}{mc^2}\Delta\,. \qquad (2)$$

On the assumption that true absorption is the predominant process equation (2) can be used to calculate $\Delta$ from the empirical value for $\mu_a$ which is reliably known for most atoms for many wave lengths.

The structure factor corresponding to $f'$ is $F'_H = F_H + i\Psi_H$, where $F_H$ is associated with the $f$'s and $\Psi_H$ with the $\Delta$'s. It is convenient to write $F_H = \Sigma F_j$, $\Psi_H = \Sigma\delta_j F_j$, $F_j$ being the contribution to $F_H$ due to the atoms of the $j$th chemical species. It is readily shown that

$$P_H \equiv \tfrac{1}{2}\{|F'_H|^2 + |F'_{\bar{H}}|^2\} = |F_H|^2 + |\Psi_H|^2 =$$
$$= \Sigma\Sigma(1 + \delta_j\delta_k)|F_j|\,|F_k| \cos(\alpha_k - \alpha_j) \qquad (3a)$$

$$D_H \equiv |F'_H|^2 - |F'_{\bar{H}}|^2 = 4F_H|\Sigma\delta_j|F_j| \sin(\alpha - \alpha_j) =$$
$$= 2\Sigma\Sigma(\delta_j - \delta_k)\,|F_j|\,|F_k| \sin(\alpha_k - \alpha_j) \qquad (3b)$$

where $\alpha$ is the phase of $F_H$, $\alpha_j$ of $F_j$. The experimental quantity $X_H$ introduced in equation (1) is given by

$X_H = D_H/P_H$. The specific form of equation (3*b*) for two atomic species becomes $n=2$

$$D_H = 4(\delta_1-\delta_2)\, F_1|\; |F_2| \sin(\alpha_2-\alpha_1)\,. \qquad (3c)$$

Consider first equation (3*a*). Under conditions of low or moderate dispersion (quartz and Cu $K\alpha$ radiation for example) $|\Psi_H|^2$ is entirely negligible compared with $|F_H|^2$, and one may set $P_H = |F_H|^2$. In other words, the imaginary terms $\Delta_j$ may be neglected if the average intensity $\frac{1}{2}\{I_H + I_{\bar{H}}\}$ for pairs of reflections $H$ and $\bar{H}$ is used to obtain the experimental structure factors $|F_H|$. This was the procedure followed in the extinction study of quartz.

In situations of strong anomalous dispersion $|\Psi_H|^2$ is still small compared with $|F_H|^2$, but may not be negligible. At the refinement stage of a structure determination, when $|\Psi_H|^2$ can be calculated with reasonable accuracy, it becomes necessary to apply a correction to the observables $P_H$ in accordance with the relation $|F_H| = \{P_H - |\Psi_H|^2\}^{\frac{1}{2}}$.

According to equation (3*b*), $D_H$ vanishes identically for all $H$ for a centrosymmetric crystal and for an asymmetric structure of an element. For an asymmetric crystal $D_H$ may vanish for a whole class of reflections. Thus $D_H = 0$ for all reflection pairs $H0L$ in quartz and sodium chlorate type structures and for all reflection pairs $HKL$ with even $H+K+L$ in sphalerite structures.

It is important to note that $D_H$ (and $X_H$) is a function of the differences $\delta_j-\delta_k$, of which $n-1$ are independent. In general $f_j/f_k$ does not vary a great deal over the experimental range, and hence only $n-1$ of the $n$ quantities $\Delta_j$ can be deduced from the observed values $D_H$ or $X_H$. Another consequence of the functional dependence on $\delta_j-\delta_k$ is that the ratio $\Delta_k f_j/\Delta_j f_k$ rather than $\Delta_k/\Delta_j$ must be used to assess the error in neglecting the dispersion contribution of the $k$th relative to the $j$th species. Thus for quartz $\Delta_O/\Delta_{Si} = 0{\cdot}09$, but $\delta_O/\delta_{Si} = 0{\cdot}15-0{\cdot}25$.

As seen from equations (3), large values of $|X_H|$ (by definition $|X_H| \leq 2$) are theoretically possible for weak reflections no matter how small the differences $\delta_j-\delta_k$. However, the smaller the differences $\delta_j-\delta_k$, the smaller is the probability of finding large $|X_H|$ values in the experimental range. On the assumption that the structure is complex enough to provide reasonable statistics it is useful to estimate the half width of the distribution function for the $|X_H|$ values. If $\overline{|X|}$, $\bar{D}$, $\bar{P}$ are the root mean square values of $X_H$, $D_H$, $P_H$, and if $\overline{|X|} \simeq \bar{D}/\bar{P}$, one has

$$\overline{|X|} \simeq \frac{\Sigma\Sigma(2N_jN_k)^{\frac{1}{2}}|\delta_j-\delta_k|f_jf_k}{\Sigma N_jf_j^2} \qquad (4a)$$

$n=2$

$$\overline{|X|} \simeq \frac{(8N)^{\frac{1}{2}}|\delta_1-\delta_2|f_1f_2}{f_1^2+Nf_2^2} \qquad (4b)$$

where $N_j$ is the number of atoms of species $j$ in the chemical formula and $N = N_2/N_1$. Clearly, if $\overline{|X|}$ is greater than the accuracy of the intensity measurements, it means that the quantities $D_H$ will be measurable for most of the reflection pairs.

## The quartz data

With Cu $K\alpha$ radiation there are 112 distinct reflection pairs of quartz in the experimental range. By symmetry $X_H = 0$ for 53 of these pairs, and the average value of $|X_H|$ for the remainder is 0·07 with extreme values of $X_H$ ranging from $-0{\cdot}41$ to $+0{\cdot}51$. The mean value of $|X_H|$ for all reflection pairs (including those with $X_H = 0$) is thus in good agreement with equation (4*b*).

The complete set of dispersion data for quartz is presented in Table 1. It is seen that seven reflection pairs have $|X_H| \geq 0{\cdot}20$, and these observations were used to determine experimentally the quantity $\Delta_{Si} - \Delta_O f_{Si}/f_O$ with the results shown in Table 2. According to any dispersion theory $\Delta_O/\Delta_{Si} \simeq \lambda_{Si}^2/\lambda_O^2 = 0{\cdot}09$, where $\lambda_{Si}$ and $\lambda_O$ are the $K$ critical absorption wave lengths. Thus the results of Table 2 give $\Delta_{Si} = 0{\cdot}31 \pm 0{\cdot}01$, $\Delta_O = 0{\cdot}028$.

Table 1. *Dispersion data for quartz*

| | $100X_H$ | | | $100X_H$ | |
|---|---|---|---|---|---|
| *HKL* | obs. | calc. | *HKL* | obs. | calc. |
| 110 | 3 | 6 | $31\bar{2}$ | −2 | −3 |
| 111 | 21 | 20 | 313 | 11 | 8 |
| 112 | 3 | 1 | $31\bar{3}$ | 0 | 0 |
| 113 | −3 | −5 | 314 | 5 | 3 |
| 114 | −2 | −4 | $31\bar{4}$ | 5 | 5 |
| 115 | −3 | −5 | 315 | 1 | −3 |
| 116 | 0 | −2 | $31\bar{5}$ | 2 | 6 |
| 210 | 22 | 22 | 320 | 2 | 0 |
| 211 | 5 | 4 | 321 | −1 | −3 |
| $21\bar{1}$ | 0 | −1 | $32\bar{1}$ | 0 | −2 |
| 212 | 8 | 7 | 322 | 5 | 1 |
| $21\bar{2}$ | 2 | −1 | $32\bar{2}$ | 10 | 11 |
| 213 | 2 | 1 | 323 | 51 | 56 |
| $21\bar{3}$ | −7 | −8 | $32\bar{3}$ | −41 | −44 |
| 214 | 1 | −2 | 324 | −1 | −2 |
| $21\bar{4}$ | −33 | −25 | $32\bar{4}$ | 0 | 2 |
| 215 | −18 | −19 | 410 | 5 | 3 |
| $21\bar{5}$ | −2 | −1 | 411 | 4 | 3 |
| 216 | −15 | −19 | $41\bar{1}$ | −2 | −1 |
| $21\bar{6}$ | 0 | 3 | 412 | 0 | −1 |
| 220 | −2 | −4 | $41\bar{2}$ | −3 | −4 |
| 221 | 0 | −2 | 413 | −3 | −3 |
| 222 | −37 | −35 | $41\bar{3}$ | 0 | 0 |
| 223 | 6 | 3 | 330 | 3 | 0 |
| 224 | 5 | 3 | 331 | 6 | 5 |
| 225 | 3 | 3 | 332 | −30 | −30 |
| 310 | −1 | −2 | 420 | 1 | 3 |
| 311 | 7 | 4 | 421 | 0 | 2 |
| $31\bar{1}$ | −5 | −7 | $42\bar{1}$ | 5 | 9 |
| 312 | 10 | 8 | | | |

Table 2. *Experimental values for* $\Delta_{Si}$

| *HKL* | $100X_H$ | $\Delta_{Si} - \Delta_O f_{Si}/f_0$ | $\Delta_{Si}$ |
|---|---|---|---|
| 111 | 21 | 0·26 | 0·31 |
| 210 | 22 | 0·25 | 0·31 |
| $21\bar{4}$ | −33 | 0·30 | 0·38 |
| 222 | −37 | 0·25 | 0·33 |
| 323 | 51 | 0·20 | 0·28 |
| $32\bar{3}$ | −41 | 0·21 | 0·29 |
| 332 | −30 | 0·23 | 0·31 |

These experimental $\Delta$-values are much smaller than those given in *International Tables for X-ray Crystallography* (1962) ($\Delta_{\mathrm{Si}}=0{\cdot}4$, $\Delta_{\mathrm{O}}=0{\cdot}1$), slightly smaller than obtained from equation (2) ($\Delta_{\mathrm{Si}}=0{\cdot}33$, $\Delta_{\mathrm{O}}=0{\cdot}035$) and in excellent agreement with the values ($\Delta_{\mathrm{Si}}=0{\cdot}30$, $\Delta_{\mathrm{O}}=0{\cdot}028$) calculated from Hönl's (1933) theory.

The last column of Table 1 gives the calculated values of $X_H$ for all reflection pairs using $\Delta_{\mathrm{Si}}=0{\cdot}31$, $\Delta_{\mathrm{O}}=0{\cdot}028$. It is seen that the agreement between theory and experiment is satisfactory. Thus the failure of Smith & Alexander to report dispersion effects for quartz remains unexplained.

## The dispersion function

Dispersion in X-ray diffraction theory can be treated formally by using an equivalent electron distribution function $\Omega'=\Omega_0+\chi+i\sigma=\Omega+i\sigma$, where $\chi+i\sigma$ is the dispersion correction. If it is assumed that the dispersive electrons are contained in volumes of linear dimensions small compared to the wave length, $\Delta_j=\int\sigma dv$, where the integral is over the crystal domain of a single atom of species $j$.

For the correlation function

$C(\mathbf{r})=\int\Omega'(\mathbf{t})\Omega'^*(\mathbf{t}+\mathbf{r})dv$ one finds

$$C(\mathbf{r})=P(\mathbf{r})+iD(\mathbf{r}) \tag{5a}$$

$$\begin{aligned}P(\mathbf{r})&=\int\Omega(\mathbf{t})\Omega(\mathbf{t}+\mathbf{r})dv+\int\sigma(\mathbf{t})\sigma(\mathbf{t}+\mathbf{r})dv=\\&=V^{-1}\Sigma P_H\cos 2\pi\mathbf{H}\,.\,\mathbf{r}\,,\end{aligned} \tag{5b}$$

$$\begin{aligned}D(\mathbf{r})&=\int\{\sigma(\mathbf{t})\Omega(\mathbf{t}+\mathbf{r})-\sigma(\mathbf{t}+\mathbf{r})\Omega(\mathbf{r})\}dv=\\&=V^{-1}\Sigma D_H\sin 2\pi\mathbf{H}\,.\,\mathbf{r}\,.\end{aligned} \tag{5c}$$

Clearly, $P(\mathbf{r})$ is a slightly modified Patterson function, while $D(\mathbf{r})$, the dispersion function, measures the difference in the correlation of $\sigma$ with $\Omega$ for $\mathbf{r}$ and $-\mathbf{r}$.

The Fourier expansion of the dispersion function was first introduced by Okaya, Saito & Pepinsky (1955), and as pointed out by them $D$ has extrema for $\mathbf{r}=\mathbf{r}_j-\mathbf{r}_k$ corresponding to vectors between unlike atoms. The integral $\int Ddv$ extended over an isolated maximum or minimum gives $\int Ddv=\Delta_j(Z_k+\Delta'_k)-\Delta_k(Z_j+\Delta'_j)\simeq\Delta_jZ_k-\Delta_kZ_j$, and for the corresponding ratio $\int Ddv/\int Pdv\simeq\Delta_j/Z_j-\Delta_k/Z_k$. Thus the dispersion function gives quite different information about the structure than does the Patterson function; but the dispersion function is much simpler than the Patterson function because there are no extrema corresponding to vector separations between like atoms.

As suggested by Okaya *et al.*, the Fourier synthesis of equation (5*c*) provides a new, powerful method for the determination of complex, asymmetric structures. Indeed, in an extreme situation with one molecule $\mathrm{XY}_N$ per cell, with Y any atom B, C, N, O, F, $\delta_{\mathrm{X}}\gg\delta_{\mathrm{Y}}$ and $N=10-10^4$, the dispersion function would give the complete structure of the crystal. The theoretical considerations of this article have shown that it is not at all necessary to make the intensity measurements under conditions of pronounced anomalous dispersion (which introduce errors due to high absorption) to obtain the dispersion function with reasonable accuracy. In confirmation of this statement Fig. 1 shows the dispersion function for quartz at the level $z=0{\cdot}119$ as obtained from the measured $D_H$ values. The maxima represent Si–O, the minima O–Si vectors.

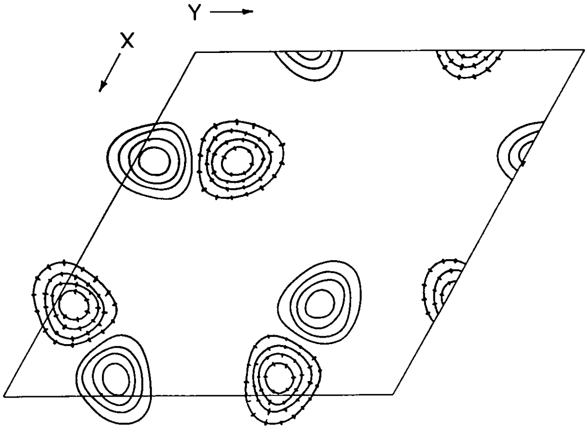

Fig. 1. The dispersion function for quartz at the level $z=0{\cdot}119$. The maximum at $x=0{\cdot}943$, $y=0{\cdot}266$ corresponds to the vector Si(1)–O(1). The other maxima and minima are related to it by symmetry.

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