Acta Cryst. (1978). A**34**, 43–47

The Measurement of the Real Part of Anomalous Scattering

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(*Received* 28 *May* 1977; *accepted* 5 *July* 1977)

The real part, f' of the anomalous dispersion correction to atomic structure factors was measured by using *Pendellösung* fringes for Si 220 and $\bar{2}\bar{2}0$ reflections in the wavelength range from Cu $K\alpha_1$ to Rh $K\alpha_1$. In order to avoid ambiguity in the Thomson-scattering term due to the nature of the bonding, the quantity $(f'_X - f'_{Ag})$ was compared with the available theoretical calculations. In this expression, f'_X and f'_{Ag} are the corrections for radiation X and Ag $K\alpha_1$, which is used as the standard, respectively. The present experimental results fit best the values calculated by Cromer & Liberman [*J. Chem. Phys.* (1970), **53**, 1891–1898].

1. Introduction

Anomalous-dispersion effects attract X-ray crystallographers for various reasons. The imaginary part f'' of the correction to the atomic scattering factor f relates to normal and anomalous (Borrmann) absorption. The precise values of the real part f' of the correction term are urgently required for the purpose of accurate structure analysis. Furthermore, the complex correction $f' + if''$ can be used for the phase determination of the crystal structure factor if the values of f' and f'' are known with sufficient accuracy. These applications of the anomalous dispersion effects, as well as the fundamental interests in the X-ray dispersion theory, were discussed at the recent conference at Madrid (Ramaseshan & Abrahams, 1975).

Although its importance has been realized for a long time, many people feel that there is a lack of accurate measurements of f' values (Weiss, 1974; Cromer & Liberman, 1970). Recently, Cusatis & Hart (1975) improved this situation considerably by applying X-ray interferometry to this problem. However, it still seems necessary to collect more accurate data for various materials and in the wavelength region in which most crystallographic work is performed.

In this work, the quantity $(f'_X - f'_{Ag})$ was measured for Si in the wavelength range from Cu $K\alpha_1$ to Rh $K\alpha_1$. Here, the suffix X specifies the X-ray wavelength employed. The principle of the method is similar to that used in the accurate measurement of the ratio of structure factors by means of *Pendellösung* fringes (Yamamoto, Homma & Kato, 1968; Tanemura & Kato, 1972).

The experimental results are compared with the recent calculations of f' (Wagenfeld, 1975; Cromer, 1965; Cromer & Liberman, 1970; Cromer, 1976). The results fit best the values given by Cromer & Liberman (1970).

2. Principles

2(*a*). *Resumé of the Pendellösung method for structure-factor determination*

The basic principle of the present work is based on the accurate determination of structure factors by means of *Pendellösung* fringes (Hattori, Kuriyama, Katagawa & Kato, 1965; Tanemura & Kato, 1972; Kato, 1969) and the ratio of structure factors (Yamamoto, Homma & Kato, 1968). Here some of them are summarized.

According to the spherical-wave theory (Kato, 1974) the intensity field in the reflection plane determined by the direct and the Bragg-reflected beams is given here:

$$I_{\perp,\parallel} = A|\bar{\beta}|^2|J_0(\bar{\beta}\sqrt{x_0x_g})|^2\exp[-\mu_0(x_0 + x_g)/\sin 2\theta_B] \quad (1)$$

where $\parallel$ and $\perp$ specify two modes of X-ray polarization, parallel and perpendicular to the reflection plane respectively. Here, J_0 is the Bessel function of zeroth order, and

$$\bar{\beta} = 2r_c(\lambda/v)(C/\sin 2\theta_B)(F_{\mathbf{g}}F_{-\mathbf{g}})^{1/2}, \quad (2)$$

which depends on the mode of polarization through the polarization factor C. It is unity for the perpendicular mode and $|\cos 2\theta_B|$ for the parallel mode. The notation used in (1) and (2) is as follows: A: proportionality factor; (x_0,x_g): coordinates of the observation point P, in the oblique axes shown in Fig. 1; μ_0: linear absorption coefficient; r_c: classical radius of an electron; λ: wavelength; v: volume of unit cell; θ_B; Bragg angle; $F_{\mathbf{g}}$: structure factor.

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In the following, we are mainly concerned with the intensity along the net plane. Then,

$$\sqrt{x_0 x_g} = \rho \sin \theta_B \quad (3a)$$

$$x_0 + x_g = 2\rho \sin \theta_B \quad (3b)$$

where ρ is the distance between the entrance point E and the observation point P.

In the main part of the crystal ($\bar{\beta}\rho \sin \theta_B \gtrsim 3$), the asymptotic expression of J_0 can be used with sufficient accuracy so that

$$I_{\perp,\parallel} = (2A\bar{\beta}/\pi \sin \theta_B)(1/\rho) \cos^2 (\bar{\beta}\rho \sin \theta_B - \pi/4). \quad (4)$$

In the actual experiment, in which unpolarized X-rays are used, the intensity field is given by

$$I = \tfrac{1}{2}[I_\perp + I_\parallel]. \quad (5)$$

The section topograph is a projection of the intensity field on the exit surface of the crystal in the direction of the Bragg-reflected beam. If a wedge-shaped crystal is used as the specimen, the topograph has a triangular form. We measured the fringe positions along the bisector (y) of the top angle of the pattern as shown in Fig. 1. If the wedge form is ideal, y and ρ are related as

$$y = y_0 + \rho\Phi \quad (6)$$

where y_0 is the coordinate of the top of the triangular pattern. In the simplest case, where the exit surface is perpendicular to the reflection plane and the recording plate is placed perpendicular to the Bragg-reflected beam, the geometrical factor can be calculated by

$$\Phi = [\sin \theta_B/\sin (w/2)] \times [\cos w \cos(\theta_B - \alpha)/\cos(\theta_B + \alpha)]^{1/2} \quad (7)$$

where w is the top angle of the pattern and α is the angle between the exit surface and the reflection vector $\mathbf{g}$.

Since the intensity field is the superposition of $I_\perp$ and $I_\parallel$ in which the fringe spacings are slightly different from each other, the fringes are disturbed in the regions where the maxima of $I_\perp$ happen to be close to the minima of $I_\parallel$. Since there the fringes lose contrast, they are called fading regions. Otherwise, the fringe spacing is regular and given by

$$\Lambda^c = r_c^{-1}(\pi v/\lambda \cos \theta_B)/\text{Re}[(F_{\mathbf{g}}F_{-\mathbf{g}})^{1/2}] \quad (8)$$

on the scale of ρ.

In previous work (Hattori, Kuriyama, Katagawa & Kato, 1965), the measurable spacing, Λ, on the y scale was converted to Λ^c by using (7) for Φ, and $\text{Re}[(F_{\mathbf{g}}F_{-\mathbf{g}})^{1/2}]$ was obtained from (8). Also, the fringes in the fading region were discarded.

Fig. 1. Geometry of the section topograph.

2(b) The improvements in obtaining the ratio of $\text{Re}(F_{\mathbf{g}}F_{-\mathbf{g}})^{1/2}$

Since we need better accuracy, it is desirable to use (1) instead of the appoximation (4). Also, use of the available fringes in the fading regions, so far as they are visible, is desirable. For these reasons, the following procedures were used in the present work. First, the ρ scale is normalized by

$$x = \rho/\Lambda^c. \quad (9)$$

Then, the positions $\{x_n\}$ of the maxima and minima of I, given by (5), are computed by the condition $\partial I/\partial x = 0$, where the expressions (1) for $I_\perp$ and $I_\parallel$ were used. The Newton method was used for this purpose. The fringe positions, therefore, can be expressed by

$$y_n = y_0 + x_n \Lambda^c \Phi. \quad (10)$$

By the standard least-squares method, one can determine $\Lambda = \Lambda^c \Phi$ from the measurements of $\{y_n\}$ and the calculated values of $\{x_n\}$. Also, the standard deviation, σ_Λ, of Λ is calculated for a set of $\{y_n\}$.

We determined a pair of Λ, one for the standard radiation,* Ag $K\alpha_1$, and one for the radiation X. Thus, from (8), we obtained:

$$\frac{\mathrm{Re}[(F_{\mathbf{g}}F_{-\mathbf{g}})^{1/2}]_X}{\mathrm{Re}[(F_{\mathbf{g}}F_{-\mathbf{g}})^{1/2}]_{\mathrm{Ag}}} = \frac{\Lambda_{\mathrm{Ag}}}{\Lambda_X}\frac{\Phi_X}{\Phi_{\mathrm{Ag}}}\frac{(\lambda\cos\theta_B)_{\mathrm{Ag}}}{(\lambda\cos\theta_B)_X}. \quad (11)$$

The expression pertinent to w in (7) can be written as

$$\sqrt{\cos w}/\sin w/2 = (\tan w)^{-1}(2\cos w/2/\sqrt{\cos w}), \quad (12)$$

whereas

$$\tan w = \tan W \sin\theta_B\left[1 + \frac{\cos(\theta_B - \alpha)}{\cos(\theta_B + \alpha)}\right] \quad (13)$$

where W is the wedge angle of the specimen in the section of the net plane. Thus, one obtains

$$\Phi_X/\Phi_{\mathrm{Ag}} = \frac{\left[\dfrac{1-\tan^2 w/2}{1-\tan^2\alpha\tan^2\theta_B}\right]^{1/2}_{\mathrm{Ag}}}{\left[\dfrac{1-\tan^2 w/2}{1-\tan^2\alpha\tan^2\theta_B}\right]^{1/2}_X}. \quad (14)$$

This is nearly equal to 1. The unknown quantity W can be eliminated. Moreover, inaccurately known quantities α and w appear only in small correction terms. This is significant from the practical viewpoint.

2(*c*) *The determination of* $(f'_X - f'_{\mathrm{Ag}})$

The crystal structure factor of Si 220, including the effects of anomalous dispersion, may be given by

$$F(220) = F^\circ + 8(f' + if'') \quad (15)$$

with the origin at the center of symmetry, where F° is the structure factor due to Thomson scattering and $(f' + if'')$ are the correction terms to the atomic scattering factor due to anomalous dispersion. Here, the reasonable assumption has been made that the anomalous dispersion is independent of the nature of the bonding. On the other hand, F° is modified by the interatomic bonding. For a crystal with a center of symmetry, $F_{\mathbf{g}}$ is identical with $F_{-\mathbf{g}}$ (Zachariasen, 1945), so that

$$\mathrm{Re}[(F_{\mathbf{g}}F_{-\mathbf{g}})^{1/2}] = F^\circ + 8f'. \quad (16)$$

Thus, one can obtain

$$\frac{\mathrm{Re}[(F_{\mathbf{g}}F_{-\mathbf{g}})^{1/2}]_X}{\mathrm{Re}[(F_{\mathbf{g}}F_{-\mathbf{g}})^{1/2}]_{\mathrm{Ag}}} \fallingdotseq 1 + \frac{8}{F^\circ}(f'_X - f'_{\mathrm{Ag}}) \quad (17)$$

with sufficient accuracy.

* Hereinafter, we shall denote it simply by Ag.

By equating (11) and (17), finally, one can determine the difference $(f'_X - f'_{\mathrm{Ag}})$ as follows.

$$f'_X - f'_{\mathrm{Ag}} = \frac{F^\circ}{8}\left[\frac{\Lambda_{\mathrm{Ag}}}{\Lambda_X}\frac{\Phi_X}{\Phi_{\mathrm{Ag}}}\frac{(\lambda\cos\theta_B)_{\mathrm{Ag}}}{(\lambda\cos\theta_B)_X} - 1\right]. \quad (18)$$

Here, F° has been determined with an accuracy better than 0·2% (Tanemura & Kato, 1972; Aldred & Hart, 1973). The other terms on the right can be determined in the present experiment.

3. Experimental

The wedge-shaped specimens were prepared from a dislocation-free single crystal of Si grown along [111] by the floating-zone method. The wedge angles are adequately designed for various radiations so that the fringe spacings are wide enough for accurate measurement. The wedge angles of the specimens and the radiations are listed in Table 1. One of the wedge surfaces was perpendicular to the growth direction. After polishing with emery powder of 3 μm size for shaping the specimens, the distorted layer was etched off by HF plus HNO_3 acid.

The (220) and $(\bar{2}20)$ net planes perpendicular to the growth direction were used for taking section topographs by standard procedures. An effort, however, was made to mount the specimen on the Lang camera so that the rotation axis lay exactly on the rear surface. In this way, the same part of the specimen could be employed in a series of topographs with different radiations, including the standard radiation Ag $K\alpha_1$.

For the purpose of the present work, a fine-focused X-ray tube whose target was interchangeable was convenient. A Ge target was prepared by evaporating Ge on the Cu target.

The fringe positions $\{y_n\}$ and the top angle w of the section topograph were measured by using an optical projector equipped with x–y traverse stages and a rotation stage. The reading accuracies of the traverse and rotation stages were 1 μm and 1 min of arc respectively.

The fringe positions were independently measured four times for each plate. The fringe distance $\Lambda = \Lambda^c\Phi$ and its standard deviation σ_Λ were calculated

Table 1. *The wedge angles of the specimens and the radiations used*

Specimen	Wedge angle, W	Radiations*
1, 2, 3, 4	~20°	Mo $K\alpha_1$; Rh $K\alpha_1$; (Ag $K\alpha_1$)
5	~12	Mo $K\alpha_1$; Rh $K\alpha_1$; (Ag $K\alpha_1$)
6, 7	~6	Cu $K\alpha_1$, $K\beta$; Ge $K\beta$, $K\alpha_1$; (Ag $K\alpha_1$)
8	~6	Cu $K\alpha_1$, $K\beta$; (Ag $K\alpha_1$)

* (Ag $K\alpha_1$): standard radiation.

Table 2. *Examples of the measurement of the fringe spacing* Λ (mm)

Values in parentheses indicate the standard deviations, σ_Λ.

	Ag $K\alpha_1$ (No. 72)	Rh $K\alpha_1$ (No. 67)	Mo $K\alpha_1$ (No. 68)
I	0·15959 (9)	0·14584 (6)	0·12638 (6)
II	0·15962 (9)	0·14580 (8)	0·12640 (6)
III	0·15954 (8)	0·14584 (7)	0·12638 (6)
IV	0·15962 (9)	0·14582 (6)	0·12651 (5)

	Ge $K\beta$ (No. 255)	Ge $K\alpha_1$ (No. 256)	Cu $K\beta$ (No. 209)	Cu $K\alpha_1$ (No. 208)
I	0·2536 (3)	0·2316 (5)	0·2104 (4)	0·1925 (3)
II	0·2547 (5)	0·2308 (4)	0·2106 (4)	0·1928 (4)
III	0·2538 (6)	0·2310 (4)	0·2093 (4)	0·1925 (2)
IV	0·2541 (4)	0·2306 (2)	0·2101 (3)	0·1931 (4)

by the least-squares procedure mentioned in § 2(*b*). The examples are shown in Table 2. The mean of the standard deviation $\bar{\sigma}_\Lambda$ indicates a measure of the error in Λ due to the measurement of the fringe positions.

4. Results and discussion

The experimental values of $(f_X' - f_{Ag}')$ obtained by (18) are listed in Table 3. Here, the figures in parentheses are the errors, ε, estimated from the standard deviations, $(\bar{\sigma}_\Lambda)_X$ and $(\bar{\sigma}_\Lambda)_{Ag}$, by consideration of error propagation. There is no significant difference between the 220 and $\bar{2}\bar{2}0$ reflections for all radiations. For this reason, all data are averaged with a weight of ε^2. The figures assigned to the weighted mean with a $\pm$ sign

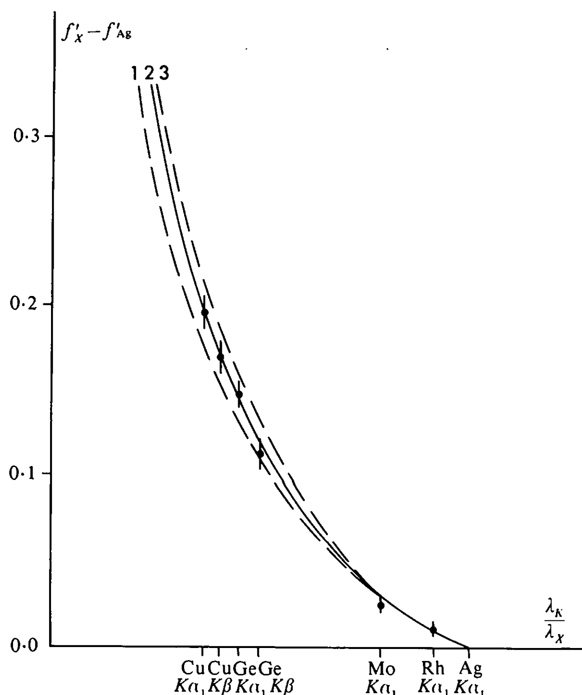

Fig. 2. Comparison of the experimental results and the theoretical calculations. λ_K: wavelength of Si $K\alpha$. λ_X: wavelength of radiation X. Curve (1) Cromer (1965). Curve (2) Cromer & Liberman (1970). Curve (3) Wagenfeld (1975).

Table 3. *The experimental values of* $(f_X' - f_{Ag}')$

All figures listed are to be multiplied by 10^{-4} for (*a*) and (*b*) and by 10^{-3} for the rest.

No.	220	$\bar{2}\bar{2}0$
(*a*) Rh $K\alpha_1$–Ag		
1	110 (55)	85 (57)
2	169 (51)	161 (69)
3	73 (52)	73 (55)
4	135 (53)	144 (47)
5	135 (127)	93 (110)
Weighted mean 118 ± 12 (24)		
(*b*) Mo $K\alpha_1$–Ag		
1	262 (58)	169 (60)
2	169 (60)	228 (69)
3	195 (66)	203 (59)
4	305 (60)	372 (58)
5	398 (118)	313 (110)
Weighted mean 248 ± 24 (24)		
(*c*) Ge $K\beta$–Ag		
6	110 (22)	137 (31)
7	110 (31)	102 (28)
Weighted mean 113 ± 8 (14)		
(*d*) Ge $K\alpha_1$–Ag		
6	144 (22)	144 (25)
7	135 (25)	144 (25)
Weighted mean 146 ± 5 (12)		
(*e*) Cu $K\beta$–Ag		
6	169 (26)	178 (25)
7	144 (25)	152 (26)
8	178 (31)	203 (26)
Weighted mean 170 ± 9 (11)		
(*f*) Cu $K\alpha_1$–Ag		
6	161 (28)	186 (25)
7	161 (26)	203 (25)
8	220 (25)	228 (28)
Weighted mean 194 ± 11 (11)		

are the standard deviation, σ, estimated on the assumption that the values obtained from the different specimens and net planes are independent. The error, ε, is due to the measurement of the fringe positions. On the other hand, the standard deviation σ includes the error due to the misalignment of the specimen and photographic plate *etc.* Nevertheless, as shown in the table, their magnitudes are comparable.

The final results of $(f'_X - f'_{Ag})$ are plotted in Fig. 2. The error bars indicate the larger of ε and σ. The results are compared with the recent theoretical calculations of Cromer (1965), Cromer & Liberman (1970) and Wagenfeld (1975). The numerical values of f'_X for Ge $K\alpha_1$ and $K\beta$ for curve 2 were specially calculated by Cromer (1976). Our results fit best curve 2 of Cromer & Liberman (1970).

In the present work, the values of $(f'_X - f'_{Ag})$ instead of f'_X were treated for two reasons. Experimentally, it is difficult to attain an accuracy in the geometrical factor, Φ, in (6) and (7), of better than 0·3%. This accuracy is not sufficient to obtain any meaningful discussion on f'. As explained in § 2(*b*), one can eliminate the error by taking the ratio of (Φ_X/Φ_{Ag}). Then, only $(f'_X - f'_{Ag})$ can be determined with sufficient accuracy.

A further, more fundamental reason, is that the real part, f', cannot be separated from the unknown modification of F° due to the bonding of the atoms. Since F° is independent of wavelength, it is reasonable to compare the experimental results of $(f'_X - f'_{Ag})$ with the dispersion theory.

The present method is very special and can be applied only to Si perfect crystals. Nevertheless, the accuracy is higher than that of any other method. It is concluded that the calculation of Cromer & Liberman (1970) is most reliable, at least for substances of low atomic number.

The authors are grateful to Dr H. Wagenfeld for general discussions on anomalous dispersion in the early stages of this work and to Professor D. T. Cromer, who kindly supplied us with his newly calculated values of f'.

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