which the average is required, but it is (i) less work and (ii) more nearly exact, *not* to weight the *hk*0 reflexions.

### Other symmetry elements

A rotation axis of order $n$ parallel to $c$ gives 00$l$ reflexions of $n$-fold intensity, while the average intensity in the rest of reciprocal space is modulated by the diffraction function $J_1(x)/x$ (Nigam & Wilson, 1980*). The enhanced intensity of the 00$l$ reflexions is compensated if the entire reciprocal lattice is considered, but (unlike the areas of the constant-$l$ planes considered above) the lengths of constant-*hk* rows intercepted by a concentric shell are not independent of *hk*, and it may be worth while to allow for the differences in intercepted length in forming averages.

There is a somewhat similar phenomenon associated with a centre of symmetry; though there are no enhanced reflexions, the average intensity in reciprocal space is modulated by a spherical Bessel function (Wilson, 1981); this effect is likely to be small compared with the larger stereochemical effects discussed there.

* In this paper there is confusion about the meaning of the symbol $s$. It is not $(2\sin\theta)/\lambda$ as is stated in the *Abstract*, but the projection of this quantity on to a plane perpendicular to the cylinder axis - this is clear from the introduction of the symbol in the context of their equation (4). Nigam & Wilson considered, in fact, only twofold axes, but their equations are valid also for the axes 3, 4 or 6 if the average atomic radius $a$ is replaced by $\sqrt{3}a/2$, $\sqrt{2}a$ or $2a$ respectively.

### References

ABRAMOWITZ, M. & STEGUN, I. A. (1970). *Handbook of Mathematical Functions.* New York: Dover.
NIGAM, G. D. (1972). *Indian J. Pure Appl. Phys.* **10**, 655-656.
NIGAM, G. D. & WILSON, A. J. C. (1980). *Acta Cryst.* A**36**, 832-833.
ROGERS, D. (1950). *Acta Cryst.* **3**, 455-464.
WILSON, A. J. C. (1950). *Acta Cryst.* **3**, 258-261.
WILSON, A. J. C. (1964). *Acta Cryst.* **17**, 1591-1592.
WILSON, A. J. C. (1981). *Acta Cryst.* A**37**, 808-810.

*Acta Cryst.* (1987). A**43**, 252-254

# On the Real Part of the Anomalous-Dispersion Term of Atomic Scattering Factors. I. Experimental Part

BY T. SAKA*

*Department of Crystalline Materials Science, Faculty of Engineering, Nagoya University, Nagoya, Japan*

AND N. KATO

*Department of Physics, Faculty of Science and Technology, Meijo University, Nagoya, Japan*

(*Received* 16 *August* 1986; *accepted* 26 *September* 1986)

### Abstract

The wavelength dependence of Si structure factors was measured by the *Pendellösung* method described in the paper of Saka & Kato [*Acta Cryst.* (1986). A**42**, 469-478] in the range from 0·8 down to 0·3 Å with an accuracy level better than 0·05% in most cases. The same conclusion as Takeda & Kato [*Acta Cryst.* (1978). A**34**, 43-47] was obtained; namely that Cromer & Liberman's theory of anomalous dispersion [Cromer & Liberman (1970). *J. Chem. Phys.* **53**, 1891-1898] is essentially correct. As a consequence Jensen's magnetic-scattering term [Jensen (1979). *Phys. Lett.* A, **74**, 41-44] is not acceptable.

* Present address: Central Research Laboratory, Daido Steel Co. Ltd, 2-30, Daido-cho, Minami-ku, Nagoya, Japan.

## 1. Introduction

In some diffraction problems an accurate value for the scattering amplitude depends on the anomalous dispersion. Examples are accurate determination of the charge density through the measurement of the crystal structure factor ($F_g$) and phase determination by the use of synchrotron radiation or any X-ray source having a continuous spectrum.

The fundamental theory of anomalous dispersion has been well established. Historically important literature can be seen in the textbook of James (1982) and the symposium report edited by Ramaseshan & Abrahams (1975). The relativistic treatment of this problem is described in the standard textbooks on quantum electrodynamics (Heitler, 1954; Akhiezer & Beresteskii, 1965). The theory was developed by

0108-7673/87/020252-03$01.50 

Cromer & Liberman (1970) (henceforth CL) in a more concrete form, and a program to calculate the numerical value ($f'+if''$) was developed by them (Cromer & Liberman, 1981).

Jensen (1979), however, pointed out that a term due to magnetic scattering is missed in the CL theory. It contributes to $f'$ and is proportional to $Z\lambda^{-2}$ ($Z$ = atomic number). The correction amounts to $4{\cdot}12\times 10^{-3}$ even for Si (a case of small $Z$) and for X-rays of wavelength 1 Å (a case of long $\lambda$).

Experimentally, however, it was confirmed by Takeda & Kato (1978) that the $\lambda$ dependence of the structure factor of Si agreed well with the CL theory in the range from 1·5 down to 0·56 Å. Because the scattering amplitude is fundamentally important in diffraction physics, it seems highly desirable to elucidate this difference between theory and experiment.

This paper reports an experiment in which the $\lambda$ dependence of Si structure factors is reexamined in the range from 0·8 down to 0·3 Å for four net planes. We arrive at the same conclusion as Takeda & Kato (1978) and find no experimental evidence for Jensen's (1979) term.

## 2. The principle of the experiment

The observable crystal structure factor can be written in the form

$$F_g = F_D + Q(f_{NT}+f'+if'')\exp(-M), \qquad (1)$$

where $F_D$ is Dawson's (1966) generalized structure factor taking into account the bonding effect of atoms in the crystal and the anisotropic thermal vibration. $F_D$ is real in the case of Si. $f_{NT}$ is the amplitude of the nuclear Thomson scattering (0·0038 for Si) and $f'+if''$ is the complex amplitude due to the anomalous dispersion. $Q$ is the structure factor of the diamond lattice (8 for even-order reflections and $4\sqrt{2}$ for odd-order reflections with the same sign as $F_D$) and $\exp(-M)$ is the ordinary Debye-Waller factor. Since the correction term to $F_D$ is sufficiently small, the inharmonicity of the thermal vibration is neglected in it.

In the present experiment, a *Pendellösung* method was used for determining the structure factor; details were described in the previous paper (Saka & Kato, 1986). In essence, the method enables us to determine the real part of $(F_gF_{-g})^{1/2}$, which turns out to be the absolute value of the real part of $F_g$ in (1) to a good approximation. It is significant that the measurement is not only accurate to better than $10^{-3}$ but also can be regarded as an absolute one. The observed values ($F^{ob}$) for various net planes and wavelengths are listed in Table 1. One comment should be made concerning the wavelength. As described in § 4.3 of Saka & Kato (1986), the wavelength drifted slightly during the course of measurements on the intensity profile so that the extremum positions of the profile had to be converted to those for a standard wavelength $\lambda$. The first column of Table 1 is this standard value.

Table 1. *Observed values of* Si *structure factor* ($F^{ob}$)

| Standard wavelength (Å) | 220 | 333 | 440 | 444 |
|---|---|---|---|---|
| 0·300 | 67·216 (6) | — | 42·710 (27) | 33·110 (9) |
| 0·350 | 67·280 (5) | — | — | — |
| 0·400 | 67·343 (5) | 32·833 (5) | 42·883 (6) | 33·176 (10) |
| 0·520 | — | — | 43·010 (5) | 33·309 (11) |
| 0·533 | — | 32·946 (6) | — | — |
| 0·600 | — | — | 43·124 (6) | — |
| 0·615 | 67·610 (7) | — | — | — |
| 0·650 | — | — | — | 33·477 (11) |
| 0·690 | — | 33·093 (22) | — | — |
| 0·700 | — | 33·103 (7) | 43·309 (14) | — |
| 0·790 | — | — | 43·448 (18) | — |
| 0·800 | 67·907 (9) | — | — | — |

Numbers in parentheses indicate the probable error.

Since a high-intensity X-ray generator (50 keV, 1200 mA) was used, we could select any wavelength in the spectrum of continuous X-rays. The data with wavelength shorter than 0·3 Å, however, seemed unreliable, because natural polarization could not be guaranteed. Furthermore, a few wavelength regions had to be avoided because the characteristic line and its escape spectrum in the solid-state detector disturbed the intensity data.

Based on these data and a set of $f'$ which is given by some means, one obtains a set of quantities

$$A_\lambda = F^{ob} - Qf'\exp(-M) \qquad (2)$$

for various $\lambda$ and a fixed net plane. Here,

$$M = 3{\cdot}877\times 10^{-3}(h^2+k^2+l^2). \qquad (3)$$

The numerical coefficient was determined in Saka & Kato's previous work (1986) by the Wilson plot with the use of the datum set of $F^{ob}$ for even-order reflections higher than 642 where it is guaranteed that $F_D$ is proportional to $\exp(-M)$. Since it is seen from (1) that $A_\lambda$ must be $\lambda$ independent for any given reflection, one can test whether the assumed set of $f'$ values is plausible or not.

## 3. Result and discussion

In Fig. 1, values of $A_\lambda/A_{0\cdot4}$ are plotted against $\lambda$, where $A_{0\cdot4}$ is the value for 0·4 Å which is available for all reflections concerned. Here, Jensen's (1979) values ($f'_J$) are assumed for $f'$. The numerical values are taken from a KEK report compiled by Sasaki (1984), in which CL values were calculated by a modified version of the program *FPRIME* of Cromer. In Fig. 2, the same is shown for Cromer & Liberman's values ($f'_{CL}$). In this case, the numerical values of $f'$ have been newly calculated by Omote up to four decimal places with the use of a program which is essentially the same as *FPRIME*. The figures are the

same to three decimal places as those calculated from Sasaki's (1984) table by the relation

$$f'_{CL} = f'_J + (\tfrac{1}{2})Z(\hbar/mc)^2(1/\lambda)^2, \qquad (4)$$

with $4{\cdot}1205 \times 10^{-3}(\text{Å}^{-2})$ for the $(1/\lambda)^2$ coefficient.

Comparing Figs. 1 and 2, one can see that the criterion of $\lambda$ independence for $A_\lambda$ is well satisfied for $f'_{CL}$ but not for $f'_J$. In Fig. 2, although a few experimental values for 440 and 444 reflections seem to be less accurate, the others meet the theoretical expectation within an accuracy of 0·05%. It is therefore concluded that the CL theory is correct as far as the $\lambda$ dependence is concerned. The magnetic-scattering correction is dubious.

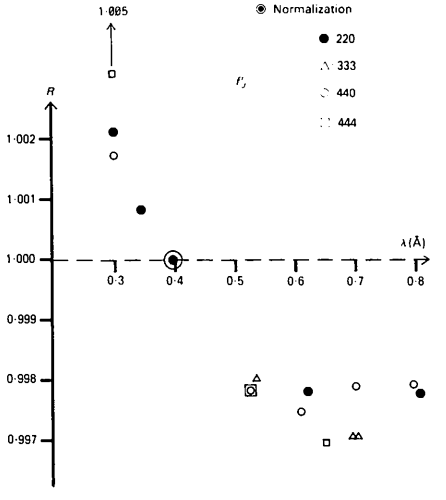


Fig. 1. $R = A_\lambda / A_{0\cdot4}$ against $\lambda$: $A_\lambda$ is defined by equation (2) with the use of Jensen's (1979) value for $f'$.

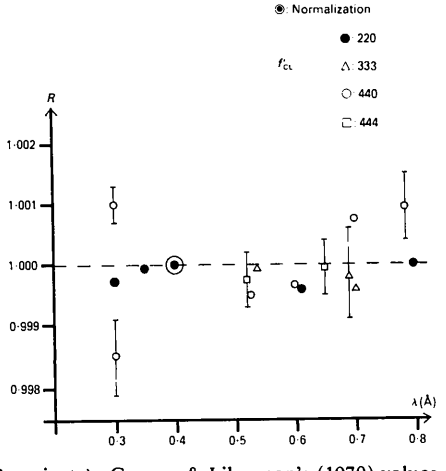


Fig. 2. $R$ against $\lambda$: Cromer & Liberman's (1970) values are used for $f'$. The error bars are due to the probable error in $F^{ob}$. They are omitted when the probable error is less than 0·025%.

A theory of anomalous dispersion with higher approximations will be presented in the following paper (Omote & Kato, 1987). According to this theory it can be shown that the magnetic-scattering term will not be observed. A minute deviation from the CL value may exist as the approximation is improved. In particular, such terms might be **g** dependent but should be $\lambda$ independent. From the principle of our experiment, the $\lambda$-independent term is irrelevant to the above conclusion.

Finally, one remark should be made about the absolute value of $f'$. Unfortunately, we do not know exactly the absolute value at the current state of the art, both from the theoretical and experimental standpoints. The CL theory gives the correction term only in the case of forward scattering ($\mathbf{g} = 0$). However, the **g** dependence would probably be very small. Another subtle problem is the effect of Compton scattering. Since the CL theory and the Omote & Kato (1987) theory both use second-order perturbations, the contribution of Compton scattering to $f'$ is missing. For these reasons, the CL value of $f'$ may need some refinements as far as the absolute value is concerned. It is highly desirable to fix this problem, particularly for obtaining the charge distribution in crystals from the observed $F_g$ values to within an accuracy of 0·05%.

The authors acknowledge Mr K. Omote for valuable discussions and the new calculation of $f'$ values. Gratitude is expressed also to the Mitsubishi Foundation for financial support.

## References

AKHIEZER, A. I. & BERESTESKII, V. B. (1965). *Quantum Electrodynamics* (translated by C. M. VOLKOFF). New York: Interscience.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.

CROMER, D. T. & LIBERMAN, D. (1981). *Acta Cryst.* A**37**, 267-268.

DAWSON, B. (1966). *Proc. R. Soc. London Ser. A*, **298**, 255-263.

HEITLER, W. (1954). *The Quantum Theory of Radiation.* Oxford Univ. Press.

JAMES, R. W. (1982). *The Optical Principles of the Diffraction of X-rays.* Woodbridge, Connecticut: Ox Bow Press.

JENSEN, M. S. (1979). *Phys. Lett. A*, **74**, 41-44.

OMOTE, K. & KATO, N. (1987). *Acta Cryst.* A**43**, 255-260.

RAMASESHAN, S. & ABRAHAMS, S. C. (1975) (Editors). *Anomalous Scattering.* Copenhagen: Munksgaard.

SAKA, T. & KATO, N. (1986). *Acta Cryst.* A**42**, 469-478.

SASAKI, S. (1984). KEK Report 83-22. National Laboratory for High Energy Physics, Tsukuba, Japan.

TAKEDA, T. & KATO, N. (1978). *Acta Cryst.* A**34**, 43-47.