

Determination of imaginary components of anomalous scattering of some elements from experimental data *

S S RAJAN and R SRINIVASAN

Department of Crystallography and Biophysics, University of Madras,
Madras 600025

MS received 8 October 1975

Abstract. Using the Bijvoet difference data reported in the literature for four compounds, *viz.*, zinc sulphide, L- α -glyceryl phosphoryl ethanolamine monohydrate, 1- β -arabinofurinosyl cytosine hydrochloride and lithium aluminium oxide, the anomalous dispersion components $\Delta f''$ of the stronger anomalous scatterer in each case is calculated accepting the theoretical values for the lighter anomalous scatterers. For MoK α radiation the values turn out to be $\Delta f''_{\text{Zn}} = 1.470$ (85), and for CuK α $\Delta f''_{\text{P}} = 0.430$ (25) $\Delta f''_{\text{Cl}} = 0.715$ (18) and $\Delta f''_{\text{Al}} = 0.264$ (21).

Keywords. Anomalous scattering; Bijvoet difference data.

1. Introduction

At present the experimental determination of real and imaginary components of x-ray anomalous scattering from elements are rather scarce. Such studies will be of interest in themselves besides being useful in checking the theoretical calculations (for recent work *see* Cromer and Liberman, 1970). As part of a programme of such experimental project recently undertaken in this laboratory an initial literature survey was made to examine accurate structure reports wherein Bijvoet difference data were also available. Apart from some of the recent accurate work which have directly led to experimental values for even as light an atom as oxygen (*see* Hope and De La Camp 1969; Engel 1972), we came across a few other accurate Bijvoet data as part of regular structure reports. In this paper we make use of these data for the calculation of the $\Delta f''$ components of a few elements. The cases covered are (a) zinc sulphide (Mair *et al* 1971), (b) L- α -glyceryl phosphoryl ethanolamine monohydrate (De Titta *et al* 1971), (c) 1- β -arabinofurinosyl cytosine hydrochloride (Sherfinski *et al* 1973). In addition we also re-examine here the calculations by Marezio (1965) in the case of (d) lithium aluminium oxide (LiAlO₂). The necessity for this arose from the fact that when a structure contains only two species of anomalous scatterers the method of least squares to determine the individual values $\Delta f''$ components as used by Marezio is inapplicable.

* Contribution No. 421 from the Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600025.

2. Method employed

It is well known (Zachariasen 1965) that experimentally determined Bijvoet ratio $X = \Delta I / \frac{1}{2} (I(\mathbf{H}) + I(\bar{\mathbf{H}}))$ or the Bijvoet difference $\Delta I = I(\mathbf{H}) - I(\bar{\mathbf{H}})$ could lead in principle, to only the relative values of the imaginary components for $n-1$ species with respect to the n th one. The Bijvoet ratio (X) is given by the Zachariasen formula (1965) which in the notation of Srinivasan (1972) takes the form

$$X = \frac{4}{[|F'_N|^2 + |F''_P|^2]} \sum_{i>j} \sum |F'_{Pi}| |F'_{Pj}| (k''_i - k''_j) \sin(a_{Pi} - a_{Pj}) \quad (1)$$

where $|F'_N|$ and $|F'_P|$ are structure factors corresponding to f' and $\Delta f''$ respectively, $f' = f_0 + \Delta f'$, $k'' = \Delta f''/f'$; $|F'_P|$ is the structure factor component of the i -th species which includes the real part of the anomalous scattering and a_P is the phase of $|F'_P|$. For the two-species case the above equation reduces to

$$X = \frac{4}{[|F'_N|^2 + |F''_P|^2]} \{(BA_1 - AB_1)k_1'' + (BA_2 - AB_2)k_2''\} \quad (2)$$

where $A = A_1 + A_2$ and $B = B_1 + B_2$, A_i 's and B_i 's being real and imaginary parts of the structure factors of the i -th species. Eq. (2) further reduces to

$$X = \frac{4(B_2A_1 - A_2B_1)}{[|F'_N|^2 + |F''_P|^2]} (k_1'' - k_2'') \quad (3)$$

which can be recast in the form

$$X = \frac{4(B_2A_1 - A_2B_1)}{[|F'_N|^2 + |F''_P|^2]f_1} (\Delta f''_{1:2}) \quad (4a)$$

where $\Delta f''_{1:2}$ is the effective value of $\Delta f_1''$ relative to species 2 given by

$$\Delta f''_{1:2} = \Delta f_1'' - \left(\frac{f_1'}{f_2'}\right) \Delta f_2'' \quad (4b)$$

We shall be mostly interested in the use of the formula (4a) above for the two-species case. Even if the structure contains more than two species, invariably one has a relatively strong anomalous scatterer and the rest may be grouped into a single average 'light anomalous scatterers.' Thus while eq. (3) is exactly applicable to ZnS and equally well for LiAlO₂ ($\Delta f''$ of Lithium is negligible), in the case of compounds (b) and (c) phosphorous and chlorine act as strong anomalous scatterers (species 1 in eq. (4)) with light atoms carbon, nitrogen and oxygen lumped into one group of 'light anomalous scatterers' which correspond to species (2) in (4a) above.

Equation (4b) now gets replaced by

$$\Delta f''_{H:L} = \Delta f''_H - \left\langle \frac{f'_H}{f'_L} \right\rangle \langle \Delta f''_L \rangle \quad (5)$$

where f''_L and $\langle \Delta f''_L \rangle$ are average values over the different species of light atoms properly weighted based on their relative proportions.

In certain cases it is possible to determine the individual values of $\Delta f''$ from the effective values using the empirical relation such as (Zachariasen 1965; Engel 1972).

$$\left(\frac{\Delta f_1''}{\Delta f_2''}\right) = \left(\frac{\lambda_2}{\lambda_1}\right)^{n-1} \quad (6)$$

with an appropriate assumption of the value of n . This was used by Zachariasen (1965) in the case of quartz. However, as has been pointed out by Engel (1972) the above is only an approximation which is reasonably valid only if the species involved are close in atomic number and also when the atoms are not heavy, since in the latter case contribution from other shells L , M , etc. are not negligible.

Although the formulae discussed above enable us to calculate $\Delta f''$ values from Bijvoet data at present two slightly different approaches are being adopted. In the first one, a large amount of data are used with appropriate weighting based on errors in estimated intensities, errors in atomic coordinates, etc. (Hall and Maslen 1966). In this case one may also use an appropriate cut off in the Bijvoet ratios and use those values of X , greater than say 5% or 10%. In the other method a smaller number of reflections with high accuracy in intensity measurement (repeated measurement for a few reflections) is used without any weighting scheme (Engel 1972). The following is the weighting scheme of Hall and Maslen (1966)* used in the four cases above. The weights attached to each reflection is inversely proportional to $\sigma^2(\Delta f'')$ where

$$\sigma^2(\Delta f'') = (\Delta F^2)^2 \left\{ \frac{(A_1^2 + B_1^2)\sigma^2(A_2) + (A_2^2 + B_2^2)\sigma^2(A_1)}{256(A_1B_2 - B_1A_2)^4} + \frac{\sigma^2(|F|^2)}{8(A_1B_2 - B_1A_2)^2} \right\} \quad (7)$$

where $\sigma^2(A) = (\pi^2 N/3)^{1/2} \overline{f\sigma(r)}/d$ where N is the number of atoms in the unit cell; $\sigma(r) = \sqrt{\sigma^2(x) + \sigma^2(y) + \sigma^2(z)}$, $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ are the errors in atomic coordinates. $\sigma^2(|F|^2) = 2|F|^2\sigma(|F|)$ where $\sigma(|F|)$ is taken as the R -factor involving amplitude $R(|F|)$. The standard deviation is given by $\overline{\sigma(\Delta f'')}/n$ where n is the total number of reflections.

Strictly in the above weighting scheme species 1 should be the anomalous scatterer and species 2, non-anomalous scatterer; however, the above weighting scheme could still be used for our purpose with the understanding that $\Delta f''$ is replaced by the effective value $\Delta f''_{1:2}$.

In all the cases *a-d*, the above weighting scheme is adopted with all the relevant quantities being taken from respective structures. It may, however, be noted that in the case of ZnS since the atoms are in fixed special position the weighting becomes a function of errors in intensities alone.

* As has been pointed out by Engel (1972) in the calculation of Hall and Maslen (1966) using the above weighting scheme, it is the effective value of $\Delta f''$ for iodine relative to light atoms that gets determined, i.e., $\Delta f''_{I:L}$.

3. Calculations

ZnS.—The data of Mair *et al* (1971) on ZnS were used to calculate $\Delta f_{\text{zn:s}}$. The Bijvoet ratios were calculated from integrated intensities from Friedel pairs. 10 out of 11 reflections for which an initial Bijvoet difference calculation showed good agreement with the observed ones were used. The weighting scheme of Hall and Maslen (1966) was used with $\sigma(r)$ (in eq. (7)) being assumed to be zero. Two sets of calculations, one using neutral scattering factors for Zn and S and the other with the assumption of $\text{Zn}^{++}\text{S}^{--}$ (international tables) were carried out. The details are given in table 1. As may be noticed, there is not much of a difference in the values for the ionic and neutral cases. It looks reasonable to assume that the average of all the four values which works out to be 1.233 ± 0.085 could be accepted as the experimental value of $\Delta f_{\text{zn:s}}''$. Equation (6) does not seem to be applicable for the present case; however, if we assume the value of $\Delta f_{\text{s}}''$ to be 0.124 (Cromer and Liberman 1970) and using eq. (4 a) and the mean values of column 1 of table 1, $\Delta f_{\text{zn}}''$ works out to be 1.470 ± 0.085 . This is in agreement with Cromer and Liberman's value (1970) for zinc for MoK α radiation.

L- α -glyceryl phosphoryl ethanolamine monohydrate ($\text{C}_5\text{H}_{14}\text{O}_6\text{NPH}_2\text{O}$)

The data for this compound are from De Titta *et al* (1971). The R-factor at the final stage is reported to be 2.9%. Bijvoet ratios were calculated as usual, and Hall and Maslen weighting scheme (1966) was adopted. There were totally 710 Bijvoet pairs available. Two distribution functions were now drawn; firstly $\Delta f_{\text{p:l}}''$ frequency distribution (figure 1 a) and secondly the weights calculated for various reflections were drawn against $\Delta f_{\text{p:l}}''$ (figure 1 b). An arbitrary cut off $\Delta f_{\text{p:l}}''$ between 0–0.7 was used and those reflections within this range (424, were analysed in regions of $\sin \theta/\lambda$. The effective values in individual ranges of $\sin \theta/\lambda$ had considerable fluctuation and it showed that the attempt to get accurate value of $\Delta f_{\text{p:l}}''$ as a function of $\sin \theta/\lambda$ will not be fruitful. In view of this only an overall mean value of $\Delta f_{\text{p:l}}''$ for the entire range was calculated. This turns out to be 0.358 ± 0.026 . The weighted average using the same data is 0.368 ± 0.025 . In view of the fact that these two agree closely, the average namely 0.363 ± 0.026 may be accepted for $\Delta f_{\text{p:l}}''$. The second term in eq. 4 b, viz., $(\Delta f_{\text{p:l}}'')$ was calculated using the formula $\langle \Delta f_{\text{l}}'' \rangle = \sum N_i \Delta f_i'' / \sum N_i$ where N_i and $\Delta f_i''$ are the number of atoms and $\Delta f''$ of the *i*-th species and it turned out to be 0.022. So also $\langle f_{\text{p}}'/f_{\text{l}}' \rangle$ turns out to be 3.06. Using these $\Delta f_{\text{p}}''$ works out to be 0.430 ± 0.026 which is in good agreement with the theoretical value of $\Delta f''(0.434)$ for CuK α (Cromer and Liberman 1970).

Table 1. Effective values of $\Delta f''$ for zinc in ZnS

| Nature of the scattering factor | $\langle f_{\text{zn}}/f_{\text{s}} \rangle$ | Weighted mean $\langle \Delta f_{\text{zn:s}}'' \rangle$ | Mean $\langle \Delta f_{\text{zn:s}}'' \rangle$ |
|---------------------------------|--|--|---|
| Ionic | 1.979 | 1.228 (0.085) | 1.234 (0.082) |
| Neutral | 2.011 | 1.225 (0.085) | 1.244 (0.080) |

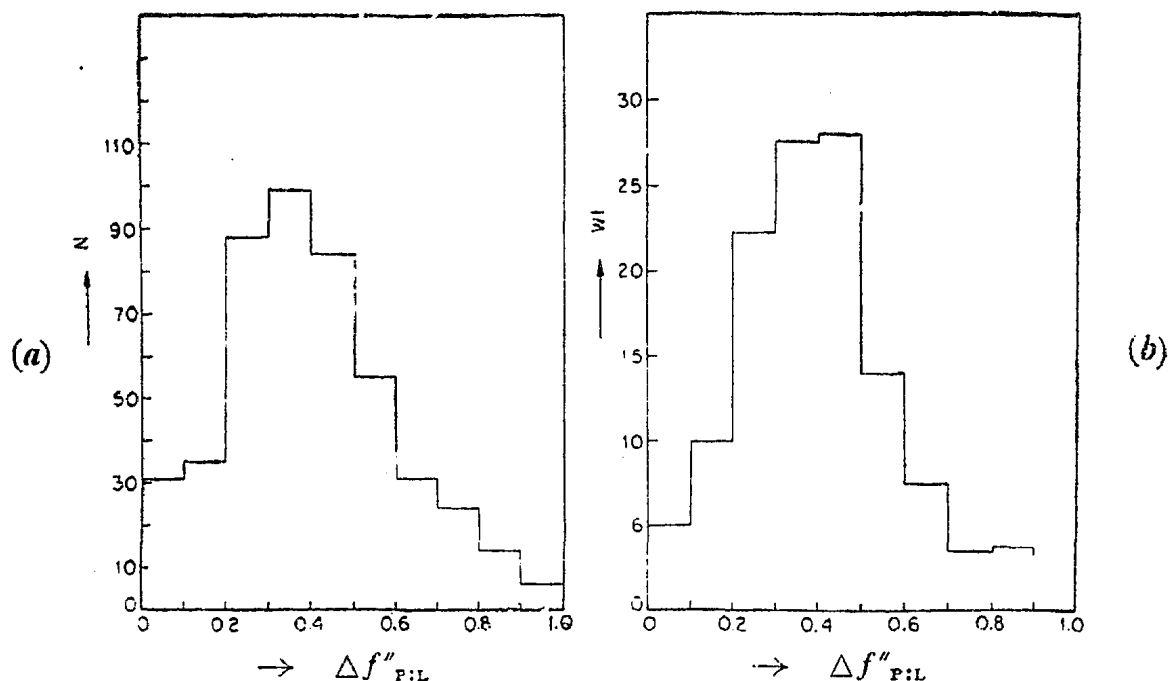


Figure 1. (a) Frequency distribution of $\Delta f''_{P:L}$ (b) Weight distribution of $\Delta f''_{P:L}$

1- β -arabinofurinosyl cytosine hydrochloride

A total number of 1210 Bijvoet pairs were available (Sherfinski *et al* 1973). The method followed was identical to the previous structure. The range of $\Delta f''_{cl:L}$ is now taken to be 0.3–1.0 within which 682 Bijvoet pairs were available. Further, to increase the accuracy, Bijvoet ratios greater than 10% were only used. Number of reflections now reduced to 432. Even with this cut-off, analysis of $\Delta f''_{cl:L}$ in ranges of $\sin \theta / \lambda$ was not meaningful; hence only an overall value for 432 reflections was attempted. The frequency distribution of $\Delta f''_{cl:L}$ and weight distribution are given in figures 2 *a* and 2 *b*. $\langle \Delta f''_L \rangle$ for this case turns out to be 0.017, and the mean value $\langle f'_{cl}/f_L \rangle$ is 3.53. The number average of $\Delta f''_{cl:L}$ is 0.667 ± 0.020 and the weight average is 0.0643 ± 0.016 . Accepting the average of these two $\Delta f''_{cl}$ calculates to be 0.715 ± 0.018 which compares well with the theoretical value of Cromer and Liberman (1970), *viz.* 0.70.

Lithium aluminium oxide.—Equation (3) can be recast in the form

$$X_i = P_i \Delta f''_1 + Q_i \Delta f''_2 \quad (8)$$

where

$$P_i = \frac{4(B_2 A_1 - A_2 B_1)}{\{|F'_N|^2 + |F''_P|^2\} f'_1} \quad \text{and} \quad Q_i = - \frac{4(B_2 A_1 - A_2 B_1)}{\{|F'_N|^2 + |F''_P|^2\} f'_2}$$

Although it appears as a straightforward case of linear equations for applying the least squares technique to arrive at $\Delta f''_1$ and $\Delta f''_2$, it may be readily shown that the method fails. This may be seen as follows: $\Delta f''_1$ and $\Delta f''_2$ are given by the following least squares solution.

$$\begin{bmatrix} \Delta f''_1 \\ \Delta f''_2 \end{bmatrix} = \frac{1}{\Delta} \begin{bmatrix} \sum Q_i^2 & -\sum P_i Q_i \\ -\sum P_i Q_i & \sum P_i^2 \end{bmatrix} \begin{bmatrix} \sum P_i X_i \\ \sum Q_i X_i \end{bmatrix} \quad (9)$$

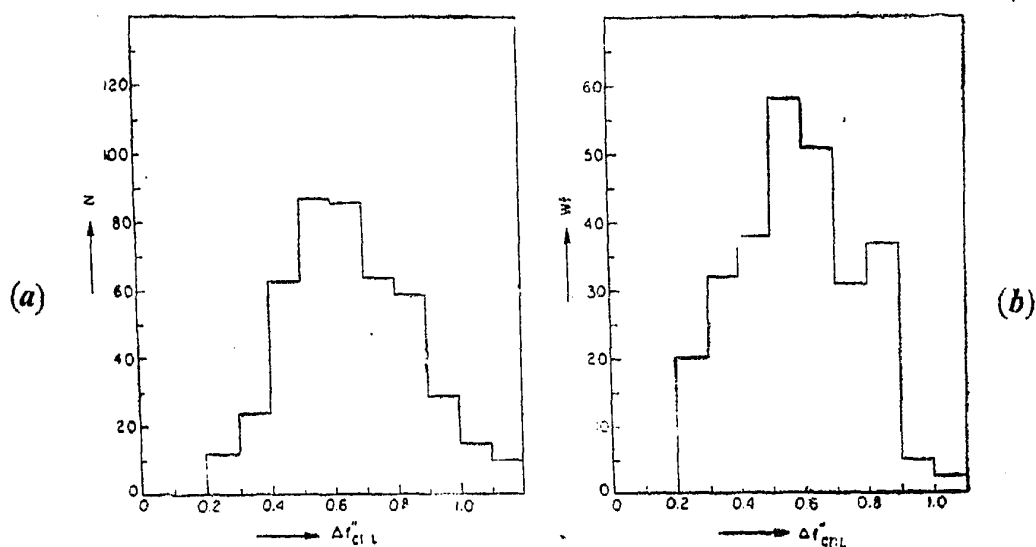


Figure 2. (a) Frequency distribution of $\Delta f''_{cl:L}$. (b) Weight distribution of $\Delta f''_{cl:L}$.

where

$$\Delta = \frac{1}{\{\sum P_i^2 \sum Q_i^2 - (\sum P_i Q_i)^2\}}$$

The value of the determinant involves a term $(f_2^i/f_2^j - f_1^i/f_1^j)$ where f_1^i and f_2^i are the atomic scattering factors for the first and second species and i and j refer to different values of $\sin \theta/\lambda$.

Thus, to the extent that the species 1 and 2 have the same shape of scattering factors and identical temperature factors, this term vanishes exactly making the right hand side of eq. (9) tend to ∞ . In actual practice to the extent that these scattering factors have similar shape the term mentioned earlier tends to take very small value and consequently the right hand side of eq. (9) becomes extremely sensitive and yields highly inaccurate values. This was in fact verified with the data of LiAlO_2 . For example with a change of $\Delta f'$ of Al from -0.1 to 0.1 changed the $\Delta f''_{\text{Al}}$ from 0.256 to 0.360 .†

In view of these considerations we have recalculated essentially $\Delta f''_{\text{Al:O}}$. The total number of reflections was 54. We used reflections for which Bijvoet ratios were greater than 5%, which turns out to be 14. Weights were calculated as usual. In view of the small number of reflections available, no distribution could be attempted. The weighted mean value of $\Delta f_{\text{Al:O}}''$ is 0.188 ± 0.021 . If the theoretical value of $\Delta f_o''$ is assumed to be 0.032 (Cromer and Liberman 1971) $\Delta f_{\text{Al}}''$ works out to be 0.264 ± 0.021 where the mean value of $\langle f_{\text{Al}}/f_o \rangle$ used was 3.294 . The theoretical value of $\Delta f_{\text{Al}}''$ for $\text{CuK}\alpha$ is 0.246 . (Cromer and Liberman 1970).

Acknowledgement

One of us (S.S.R.) thanks the University Grants Commission, India, for financial support.

† Incidentally it may be remarked that the earlier value of $\Delta f_{\text{Al}}''$ and $\Delta f_o''$ could be reproduced by us only if we use $\Delta f_{\text{Al}}' = 0.1$. However if we accept the theoretical value to be correct viz., $\Delta f'_{\text{Al}} = 0.204$, $\Delta f''_{\text{Al}}$ turns out to be 0.426 .

References

- Cromer D T and Liberman D 1970 Los Alamos Scientific Laboratory, *University of California Report LA-4403, UC-34.*
- De Titta G T and Craven B M 1971 *Nature New Biology* **233** 111
- Engel D W 1972 *Acta Cryst.* **B 28** 1496
- Hall S R and Maslen W N 1966 *Acta Cryst.* **20** 383
- Hope H and DE LA Camp U 1969 *Nature* **221** 54
- International Tables for Crystallography 1962 III Birmingham Press
- Mair S L, Prager P R and Barnea Z 1971 *J. Appl. Cryst.* **4** 169
- Marezio M 1965 *Acta Cryst.* **19** 396
- Sherfinski J and Marsh R E 1973 *Acta Cryst.* **B 29** 192
- Srinivasan R 1972 *Advances in Structure Research by Diffraction Methods* Vol. 4 (eds. W. Hoppe and R. Mason) Pergamon Press
- Zachariasen W H 1965 *Acta Cryst.* **18** 714