

taking into account anomalous dispersion. This point is extremely important for the experimental determination of the absolute structure (configuration) for light-atom structures.

For the relation between the asymmetry of  $\psi$ -scan profiles and the triplet phase to remain unambiguous some restrictions apply. The foregoing results are true if the relevant scalar products [*cf.* (3)] between the  $\pi$ - and  $\sigma$ -polarization modes are positive. If this is not the case an additional reversal of asymmetry may occur (Juretschke, 1984). These conditions must therefore be checked in order to avoid misinterpretations with respect to the triplet phase.

From the results and discussion it might be speculated that triplet phases can be determined experimentally with relatively high precision, for example, by fitting the experimental and theoretical  $\psi$ -scan profiles. However, experimentally the theoretical assumptions must then be fulfilled: ideal perfect crystal with well oriented perfect faces, definite diffraction geometry, accurately known structure-factor moduli *etc.* With specimens commonly used for X-ray crystal structure determination these requirements can hardly be fulfilled. For the measurements we use crystals with typical dimension from 0.1 to 0.5 mm and grown faces. They are bathed in the incident beam. Thus the incident radiation strikes several faces and a mixture of primary Bragg and Laue cases occurs. In spite of these adversities triplet phases can be measured with a precision of at least 45°, as will be shown in the following paper (Hümmer, Weckert & Bondza, 1990).

Experimentally the *Umweganregung* and *Aufhellung* can be evaluated by comparing  $\psi$ -scan profiles of centrosymmetrically related three-beam cases  $0/h/g$  and  $0/-h/-g$  which have triplet phases with opposite signs but constant structure-factor moduli if anomalous dispersion can be neglected. For precise phase determination however, the *Umweganregung*

or *Aufhellung* effects must be as small as possible. As can be seen from our calculations, ideal profiles result if  $|F(g)|$  and  $|F(h-g)|$  are about twice as strong as  $|F(h)|$ .

These results were reported at the 11th European Crystallographic Meeting in Vienna (Weckert & Hümmer, 1988) and in part at the Fourteenth International Congress of Crystallography in Perth (Hümmer, Bondza & Weckert, 1987; Weckert, Bondza & Hümmer, 1987).

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#### References

- BATTERMAN, B. W. & COLE, H. (1964). *Rev. Mod. Phys.* **36**, 681-717.  
 CHANG, S. L. & TANG, M. T. (1988). *Acta Cryst.* **A44**, 1065-1072.  
 EWALD, P. P. & HÉNO, Y. (1968). *Acta Cryst.* **A24**, 5-15.  
 HÜMMER, K. & BILLY, H. (1982). *Acta Cryst.* **A38**, 841-848.  
 HÜMMER, K. & BILLY, H. (1986). *Acta Cryst.* **A42**, 127-133.  
 HÜMMER, K., BONDZA, H. & WECKERT, E. (1987). *Acta Cryst.* **A43**, C222.  
 HÜMMER, K., WECKERT, E. & BONDZA, H. (1989). *Acta Cryst.* **A45**, 182-187.  
 HÜMMER, K., WECKERT, E. & BONDZA, H. (1990). *Acta Cryst.* **A46**, 393-402.  
 JURETSCHKE, H. J. (1982). *Phys. Lett.* **92A**, 183-185.  
 JURETSCHKE, H. J. (1984). *Acta Cryst.* **A40**, 379-389.  
 LAUE, M. VON (1960). *Röntgenstrahl-Interferenzen*, 3rd ed., p. 343. Frankfurt am Main: Akademische Verlagsgesellschaft.  
 MOON, R. M. & SHULL, C. G. (1964). *Acta Cryst.* **17**, 805-812.  
 PINSKER, Z. G. (1978). *Dynamical Scattering of X-rays in Crystals: Solid State Sciences 3*, edited by M. CARDONA, P. FULDE & H. J. QUEISER, pp. 433 ff. Berlin: Springer.  
 RENNINGER, M. (1937). *Z. Kristallogr.* **97**, 107.  
 SHEN, Q. & COLELLA, R. (1988). *Acta Cryst.* **A44**, 17-21.  
 TANG, M. T. & CHANG, S. L. (1988). *Acta Cryst.* **A44**, 1073-1078.  
 THORKILDSEN, G. (1987). *Acta Cryst.* **A43**, 361-369.  
 WECKERT, E., BONDZA, H. & HÜMMER, K. (1987). *Acta Cryst.* **A43**, C264.  
 WECKERT, E. & HÜMMER, K. (1988). *Z. Kristallogr.* **185**, 454.

*Acta Cryst.* (1990). **A46**, 393-402

## Direct Measurements of Triplet Phase Relationships of Organic Non-Centrosymmetric Structures using Synchrotron Radiation

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#### Abstract

Recent progress in experimental triplet phase determination by the method of three-beam diffraction for

non-centrosymmetric light-atom structures is reported. The measurements were carried out with a special  $\psi$ -circle diffractometer installed at the DORIS II storage ring in Hamburg. Experimental results

confirm the theoretical considerations. In general, the  $\psi$ -scan profiles consist of a phase-independent *Umweganregung* or *Aufhellung* part superimposed on a phase-dependent part due to the three-beam interference, which contains the phase information. Experimentally, *Umweganregung* and *Aufhellung* effects can be evaluated by comparison of the two centrosymmetrically related three-beam cases. It is shown that with moderate phase-independent effects the triplet phase can be determined with an accuracy of about  $45^\circ$ .

### 1. Introduction

In a recent paper (Hümmer, Weckert & Bondza, 1989) we reported the direct measurements of triplet phases by means of three-beam interference experiments for two non-centrosymmetric test structures with relatively small unit cells using Cu radiation from a rotating-anode generator. It was shown that the three-beam interference effect leads to typical  $\psi$ -scan profiles for triplet phases near  $0$ ,  $180$ ,  $+90$  or  $-90^\circ$ .

On the other hand, the theoretical considerations in the preceding paper (Weckert & Hümmer, 1990) show that it should be possible to achieve a higher precision in experimental triplet phase determination in spite of phase-independent *Umweganregung* and *Aufhellung* effects superimposed on the interference effect. The three-beam interference between the primary diffracted wave and the *Umweg* wave gives rise to the typical 'ideal'  $\psi$ -scan profiles which carry the phase information. It should be possible to evaluate the troublesome *Umweganregung* and *Aufhellung* effects by comparing the  $\psi$ -scan profiles of two centrosymmetrically related three-beam cases  $0/h/g$  and  $0/-h/-g$  which involve equal triples of structure-factor magnitudes but triplet phases of opposite sign if anomalous-dispersion effects can be neglected. However, because of the experimental systematic uncertainties the *Umweganregung* and *Aufhellung* should be avoided. Thus, the basic requirement for this procedure is that the primary, secondary and the coupling reflections have nearly equal intensities.

Our method of quantitative determination of triplet phases is in some important aspects different from that proposed by Shen & Colella (1988) and Tang & Chang (1988).

In the experiments of Shen & Colella the intensity change of very weak primary reflections caused by strong multiple reflections is used. The phase information is obtained from the asymmetry in the wings of the multiple-reflection peaks which are dominated by strong *Umweganregung*. The asymmetry decreases with decreasing cosine of the triplet phase. So the authors stated that only  $\cos \phi$  can be determined.

In the paper of Tang & Chang (1988) the very weak 222 reflection of GaAs was used as the primary reflection with otherwise strong secondary and coupling

reflections. As a consequence strong *Umweganregung* peaks occur. The authors claim that it is possible to evaluate the *Umweganregung* by calculation of a 'kinematical profile' with a scaling factor  $C$  which could only be determined with large errors, clearly demonstrated in their Fig. 3. As the determination of  $C$  as well as the shift between the experimental and the so-called 'kinematical' profile are the crucial points, we cannot understand the excellent agreement between the experimentally determined and true triplet phases (Table 2 of Tang & Chang). In particular, for  $\lambda = 1.1236 \text{ \AA}$  strong anomalous-dispersion effects are to be expected as this wavelength is close to the  $K$  absorption edges of gallium and arsenic. There are some questions about the definition of the triplet phase used by Tang & Chang [*cf.* comments on this paper by Hümmer & Weckert (1990)] in this case.

In order to test the power of our method as a tool for quantitative triplet phase determination, we made measurements with several organic non-centrosymmetric structures up to a unit-cell volume of nearly  $3000 \text{ \AA}^3$ . We used synchrotron radiation because of its high collimation and the possibility of tuning the wavelength. Thus, overlapping and interaction of adjacent three-beam cases could be avoided.

The purpose of this paper is to show that triplet phases can be determined experimentally with an accuracy of about  $45^\circ$ . This is satisfactory for the combination of measured triplet phases with direct methods for crystal structure determination.

### 2. Experimental

The special  $\psi$ -(six-)circle diffractometer described earlier (Hümmer, Bondza & Weckert, 1987) was installed at the DORIS II storage ring at HASY-LAB/DESY, Hamburg. The angular resolution of the crystal circles was improved to  $2 \times 10^{-4}^\circ$ .

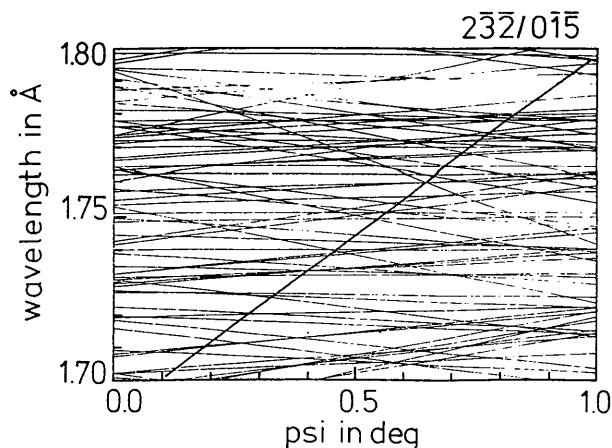


Fig. 1. Dependence of  $\psi$  positions of multiple-beam points on wavelength for L-asparagine.

Table 1. *List of structures investigated*

Name	Chemical formula	Space group	Unit-cell volume (Å <sup>3</sup> )	Z
L-Asparagine monohydrate (1)	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	646	4
Benzil (2)	C <sub>14</sub> H <sub>10</sub> O <sub>2</sub>	P3 <sub>2</sub> 21	832	3
L-Ascorbic acid (3)	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	P2 <sub>1</sub>	700	4
Raffinose pentahydrate (4)	C <sub>18</sub> H <sub>32</sub> O <sub>16</sub> ·5H <sub>2</sub> O	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	2634	4
L-Glutamic acid (5)	C <sub>5</sub> H <sub>9</sub> NO <sub>4</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	623	4
Mezanon (6)	C <sub>11</sub> H <sub>12</sub> ClNO <sub>3</sub> S	P2 <sub>1</sub>	1235	4
PALU (7)	C <sub>27</sub> H <sub>26</sub> F <sub>2</sub> O <sub>4</sub>	P1	1171	2
Propafenon (8)	C <sub>21</sub> H <sub>27</sub> NO <sub>3</sub> ·HCl	P2 <sub>1</sub>	1997	4
Butafenon (9)	C <sub>23</sub> H <sub>31</sub> NO <sub>3</sub> ·C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> ·H <sub>2</sub> O	P2 <sub>1</sub>	1431	2
DIMA (10)	C <sub>20</sub> H <sub>24</sub> N <sub>2</sub> ·C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>	P2 <sub>1</sub>	1105	2

The fractional atomic coordinates were taken from: (1) Kartha & De Vries (1961); (2) Brown & Sadanaga (1965); (3) Hvoslef (1968) [warning: in this paper a left-handed coordinate system is used]; (4) Berman (1970); (5) Lehmann & Nunes (1980); (6) Burzlaff (1988); (7) Paulus (1988); (8) Weckert (1990a); (9) Weckert (1990b); (10) Weckert (1990c).

The radiation was taken from a bending magnet at 3.65 GeV. A Ge(111) double-crystal monochromator with two independent rotatable crystals was used to adjust the wavelength between 0.7 and 3.0 Å. The wavelength setting was fully computer controlled. A new wavelength could be selected within 1 min with a reproducibility of  $2 \times 10^{-4}$  Å. The position of the outgoing beam remained constant, because the first monochromator crystal can be moved along the white beam by means of a translation table. The cross section of the beam was  $1 \times 1$  mm.

For each three-beam case the wavelength is selected so that there is no adjacent multiple reflection position within a  $\psi$ -angular range of  $\pm 0.1^\circ$ . An example for L-asparagine is shown in Fig. 1. Each straight line represents a three-beam position for the primary reflection  $2\bar{3}\bar{2}$  as a function of wavelength. To avoid confusion they are not indexed. If the three-beam case  $000/2\bar{3}\bar{2}/01\bar{5}$  is to be measured (strong solid line in Fig. 1), the wavelengths 1.729 or 1.786 Å should be selected. The distance on the  $\psi$  scale to the next three-beam case is then optimal. A computer program calculates all possible three-beam positions for a given primary reflection for a full  $360^\circ$   $\psi$  rotation in a selected wavelength interval and determines the optimum wavelength for the selected three-beam case.

The second criterion for selecting a suitable three-beam case concerns the structure-factor moduli or the intensities of the reflections involved. As the synchrotron radiation is polarized horizontally the structure factors were corrected for polarization factors valid for the two-beam diffractions  $0/h$  for the primary reflection,  $0/g$  for the secondary reflection and  $g/h - g$  for the coupling reflection. The reduced structure-factor moduli of the secondary and the coupling reflections should be twice as large as that of the primary reflection. In our experience *Umweganregung* and *Aufhellung* are then as small as possible.

The measuring routines run on a PDP 11/73. The procedure has been described previously (Hümmel, Weckert & Bondza, 1989). The crystals used for the

measurements were non-cut, with grown faces. The crystal dimensions vary from 0.1 to 0.3 mm. The organic non-centrosymmetric structures used are listed in Table 1.

Because of the instability of the synchrotron-radiation source, one observes intensity fluctuations of the primary reflection particularly when the half width of the primary reflection is very small. To smooth out these fluctuations we use a multiple scan technique. Each  $\psi$ -scan profile is the sum of many very fast scans with a typical measuring time of 0.05 s per step. The intensity fluctuations which can be seen in the measured profiles are not due to counting statistics but they are caused by source instability.

### 3. Experimental results

The profiles plotted in this paper refer to so-called 'in-out'  $\psi$  scans, *i.e.* for  $\psi < 0$  the second reciprocal-lattice vector terminates inside the Ewald sphere, for  $\psi > 0$  it lies outside.  $\psi = 0$  marks the three-beam position. It is experimentally fixed by the maximum of the secondary reflection profile measured by means of a  $\psi$  scan. This can be done because the detector can be moved to any position on a hemisphere above the horizontal scattering plane of the primary reflection by means of the detector circles  $\theta$  and  $\nu$ . This control of the three-beam position is extremely useful if the reciprocal lattice is very dense because it ensures that the selected three-beam case is measured.

In each figure the indices of the primary  $h$  reflection and the secondary  $g$  reflection as well as the triplet phase sum for this three-beam case is inserted. In each figure caption the name of the structure, the wavelength used for this measurement and the structure-factor moduli corrected for the geometrical coupling (polarization) factors for  $\pi$ -polarized incident beam in the sequence  $a|F(h)|$ ,  $b|F(g)|$ ,  $c|F(h-g)|$  are given, with

$$a = \pi_0 \cdot \pi_h = \cos 2\vartheta, \quad b = [(\pi_0 \cdot \pi_g)^2 + (\pi_0 \cdot \sigma_g)^2]^{1/2}, \\ c = [(\pi_g \cdot \pi_h)^2 + (\sigma_g \pi_h)^2]^{1/2}.$$

The  $\pi$ 's and  $\sigma$ 's are unit vectors for the polarization components. The  $\pi$ 's are parallel to the diffraction plane (horizontal plane) of the primary reflection. The  $\sigma$ 's are perpendicular to the corresponding  $\pi$ 's and to the corresponding wave vectors.

First of all it should be proved experimentally that the triplet phase which can be determined from the  $\psi$ -scan profile of the three-beam case  $0/h/g$  is given by  $\varphi = -\varphi(h) + \varphi(g) + \varphi(h-g)$ , equivalent to  $\phi = \varphi(-h) + \varphi(g) + \varphi(h-g)$ , neglecting anomalous dispersion. In Figs. 2(a) and (b) the  $\psi$ -scan profiles of two centrosymmetrically related three-beam cases  $0/h/g$  and  $0/-h/-g$  are shown. Depending on whether the triplet phase is near  $-90^\circ$  (Fig. 2a) or near  $+90^\circ$  (Fig. 2b) one observes a constructive or destructive interference pattern, respectively. These patterns are reversed as shown in Figs. 2(c) and (d) (for *Aufhellung* see § 3C) for the couple of three-beam cases  $0/g/h$  and  $0/-g/-h$ , where the primary and secondary reflections are interchanged. In this case the triplet phase is given by  $\phi' = -\varphi(g) + \varphi(h) + \varphi(g-h) = -\phi$ . In measuring these pairs we benefit from the polarization of the synchrotron radiation.

The primary reflection is more influenced by the polarization factor than the secondary, because the first is observed in the horizontal scattering plane. So in both cases the secondary reflection is stronger if  $F(h)$  and  $F(g)$  have nearly the same magnitude.

The second point to be stressed here is that the triplet phase can be experimentally determined from the three-beam  $\psi$ -scan profiles with an accuracy of about  $45^\circ$  in spite of *Aufhellung* or *Umweganregung* effects. The trick is to compare the  $\psi$ -scan profiles of the pair of the two centrosymmetrically related three-beam cases  $0/h/g$  and  $0/-h/-g$ . This procedure was tested with the structures listed in Table 1. The most important results are reported here.

### A. Ideal profiles

In a three-beam case the  $h$  beam scatters into the  $g$  beam and *vice versa*. This must occur because of the conservation of energy principle, independent of their phase relationship. If this phase-independent interaction is well balanced then so-called 'ideal profiles' governed by the interference effect are

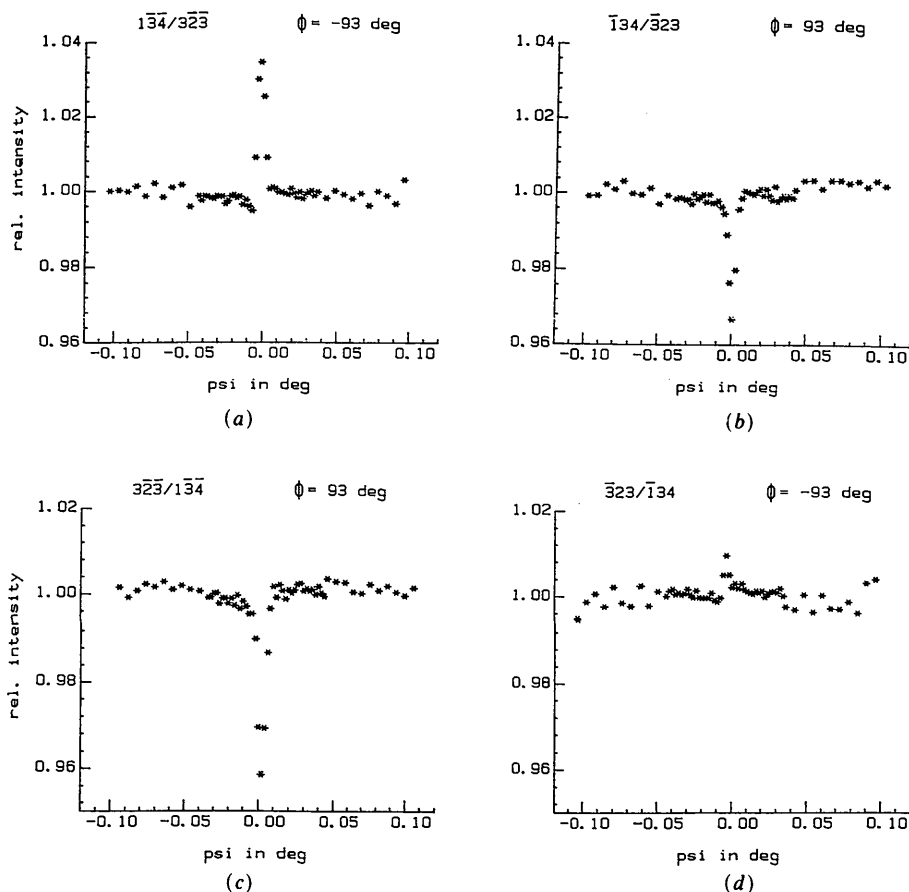


Fig. 2.  $\psi$ -scan profiles for two pairs of centrosymmetric three-beam cases with primary and secondary reflections interchanged. Benzil,  $\lambda = 1.681$  Å; (a) and (b):  $a|F(\bar{1}34)| = 12$ ,  $b|F(\bar{3}23)| = 15.5$ ,  $c|F(211)| = 24$ ; (c) and (d):  $a|F(\bar{3}23)| = 12.5$ ,  $b|F(\bar{1}34)| = 13.5$ ,  $c|F(\bar{2}\bar{1}\bar{1})| = 25$ .

observed. An example for triplet phases near  $\mp 90^\circ$  was given in Figs. 2(a) and (b) where the relative change of the two-beam intensity is  $\pm 3.5\%$ . An ideal  $180^\circ$  profile is shown in Fig. 3(a).

For a triplet phase near  $45^\circ$  we expect an intermediate profile, between ideal  $0$  and  $90^\circ$  profiles. We expect a smaller increase, but a deeper decrease of the two-beam intensity than in the case of an ideal  $0^\circ$  profile. The opposite behaviour is expected for a  $-45^\circ$  profile. This behaviour can also be deduced from the phase-

vector diagram of Hümmér & Billy (1986). Such profiles are shown in Fig. 3(b). The small dip on the right-hand side of the  $47^\circ$  profile is due to a small mosaic block. This is also observed in the two-beam profile of the  $\bar{1}2\bar{1}$  reflection by scanning around the  $\psi$  axis.

Equivalent arguments hold for three-beam  $\psi$ -scan profiles with triplet phases near  $\pm 135^\circ$ . Intermediate profiles between ideal  $\pm 90$  and  $180^\circ$  profiles should result. Such profiles are shown in Fig. 3(c).

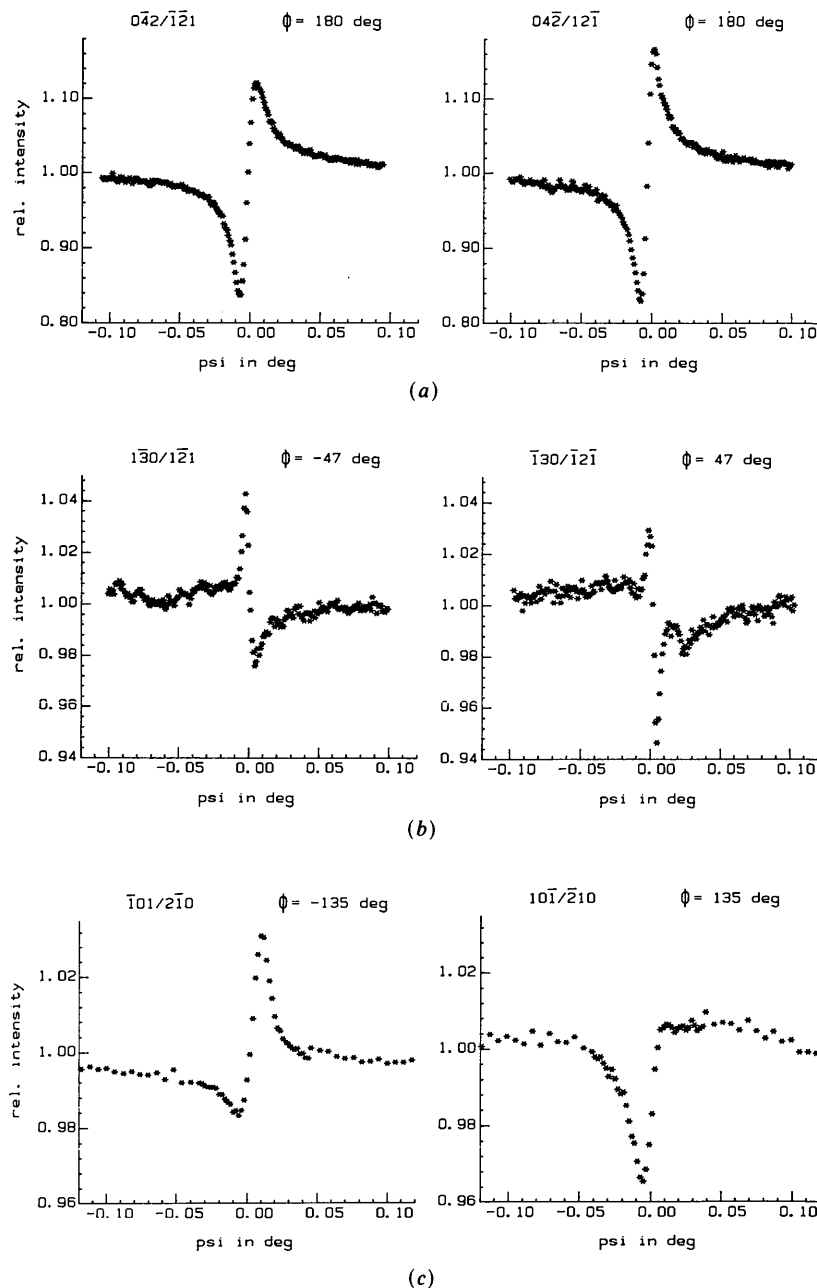


Fig. 3. 'Ideal'  $\psi$ -scan profiles. (a) L-Glutamic acid,  $\lambda = 2.100 \text{ \AA}$ ; 22, 52, 52. (b) DIMA,  $\lambda = 1.681 \text{ \AA}$ ; 47, 61, 35. (c) L-Ascorbic acid,  $\lambda = 1.529 \text{ \AA}$ ; 20, 44, 32.

### B. Profiles with *Umweganregung*

According to the theoretical considerations in the preceding paper (Weckert & Hümmer, 1990) *Umweganregung* effects should occur if the intensity of the secondary reflection is much higher than that of the primary reflection provided that the coupling reflection is approximately of the same magnitude as the primary one. In this case the phase-independent interaction results in a narrow symmetric profile enhancing the two-beam intensity. This *Umweganregung* peak ( $\Delta I$  curve of the preceding paper) is superimposed on the ideal profiles. As a consequence, for the centrosymmetric pair of  $0^\circ$  profiles [shown in Fig. 4(a)] and  $180^\circ$  profiles no significant difference should occur. The pair of  $\psi$ -scan profiles with triplet phases near  $\pm 45^\circ$  (Fig. 4b) must show different features. The sum of a small *Umweganregung* profile and an ideal  $+45^\circ$  profile may give a resultant profile that looks very similar to an ideal  $0^\circ$  profile. But if we compare it with the  $-45^\circ$  profile, significant differences can be seen: the relative enhancement is much stronger than the relative decrease of the two-beam intensity. Thus, this pair of  $\psi$ -scan profiles can be clearly discriminated from  $0^\circ$  profiles.

The disappearance of the asymmetry is the typical feature for three-beam profiles with triplet phases near  $\pm 90^\circ$ . In Fig. 4(c) we have selected an example where the *Umweganregung* overcompensates the destructive interference effect due to the triplet phase near  $+90^\circ$ . In spite of the strong *Umweganregung* of  $+26\%$  the  $+90^\circ$  and  $-90^\circ$  profiles can be discriminated. The interference effect is about  $\pm 5\%$ .

For  $\psi$ -scan profiles with triplet phases near  $\pm 135^\circ$  equivalent arguments hold as for  $\pm 45^\circ$  profiles. The asymmetry of ideal  $\pm 45^\circ$  profiles compared with that of ideal  $\pm 135^\circ$  profiles is reversed by a mirror line through the three-beam point  $\psi = 0$ . Thus, the asymmetry of three-beam profiles with *Umweganregung* is also reversed. An example with relatively strong *Umweganregung* is shown in Fig. 4(d). This type of centrosymmetric pair of three-beam profiles can be clearly discriminated from the couple of  $180^\circ$  profiles because of the evident differences of the  $\pm 135^\circ$  profiles that do not occur for a couple of  $180^\circ$  profiles.

### C. Profiles with *Aufhellung*

As can be seen from the sequence of profiles in Fig. 5 the profiles with *Aufhellung* can be derived by a superposition of a symmetrical decrease ( $\Delta I$  curve for *Aufhellung*) and the ideal profiles.

Fig. 2(d) shows an example where the constructive interference effect of a  $-90^\circ$  triplet phase is almost compensated by the *Aufhellung*; in Fig. 5(b) it is overcompensated. In summary, Fig. 5 shows that in case of moderate *Aufhellung* the centrosymmetric couples of  $\psi$ -scan profiles due to triplet phases

$\phi = 0^\circ \bmod 45^\circ$  ( $0 \leq |\phi| \leq 180^\circ$ ) can be clearly distinguished.

An interesting example is given in Figs. 3(a) and 5(d). Both represent the same three-beam case, but they were measured using different wavelengths. The polarization factors mainly affect the intensity of the primary reflection, as can be seen from the reduced structure factors. For the shorter wavelength, as is the case in Fig. 5(d), it is larger than in the case of Fig. 3(a). As a consequence, *Aufhellung* is observed in Fig. 5(d).

## 4. Discussion

The foregoing examples show a selection from about 300 pairs of  $\psi$ -scan profiles of centrosymmetrically related three-beam cases of different structures (see Table 1). A summary of types of observed profiles is given in Fig. 6, where the typical features are drawn schematically. The *Umweganregung* and *Aufhellung* were chosen so as to be almost equal to the interference effect. In general, the increase and decrease due to *Umweganregung* and *Aufhellung* ( $\Delta I$  curve of the preceding paper) are as sharp as the  $90^\circ$  profiles, so that only the centre of the profiles are affected. This can be seen from the  $\pm 45^\circ$  or  $\pm 135^\circ$  profiles, where in the case of *Umweganregung* the minimum and in the case of *Aufhellung* the maximum very often remains nearly constant. This is also confirmed by the calculated profiles in the preceding paper (Weckert & Hümmer, 1990).

To evaluate the *Umweganregung* or *Aufhellung* in each case the pair of profiles of centrosymmetric three-beam cases  $0/h/g$  and  $0/-h/-g$  must be measured. By means of visual comparison of the couple of measured profiles with the types given in the catalogue (Fig. 6) the triplet phases can be determined with an accuracy of about  $45^\circ$ ; that means they can be assigned to phase octants with centres at  $0^\circ \bmod 45^\circ$ .

If the *Umweganregung* or the *Aufhellung* is larger than the interference effect the error in phase determination increases. This is shown in Figs. 7 and 8. In Fig. 7 it is very difficult to discriminate between  $90^\circ$  and  $45^\circ$ . The weak minimum in the  $+48^\circ$  profile indicates a triplet phase near  $45^\circ$ . Such asymmetries can only be observed in high-quality crystals. For crystals of lower quality the difference in the asymmetry at the foot of the profiles is smeared out. On the other hand, the almost symmetric profiles indicate a triplet phase very near to  $90^\circ$ .

In Fig. 8 it is even difficult to discriminate between  $90^\circ$  and  $180^\circ$ . In the  $-174^\circ$  profile the left flank is less steep than the right one. This indicates a triplet phase that is not near  $90^\circ$ . The  $+174^\circ$  profile is almost symmetric; this indicates a triplet phase near  $90^\circ$ . Likewise, the almost equal decrease in the two-beam intensity of about 8% in each profile indicates a triplet

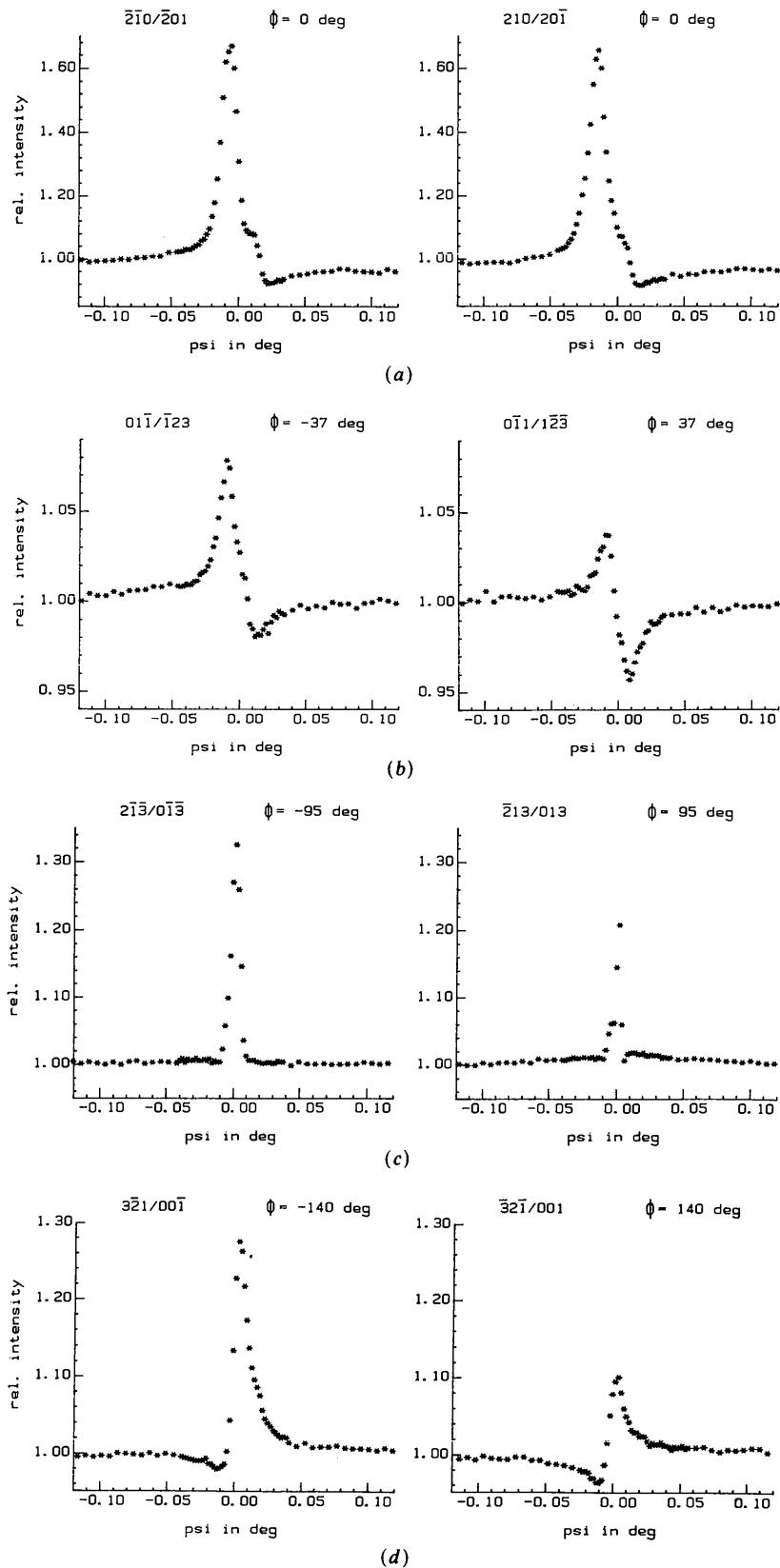


Fig. 4.  $\psi$ -scan profiles with *Umweganregung*. (a) PALU,  $\lambda = 1.761 \text{ \AA}$ ; 19, 46, 77. (b) Mezanon,  $\lambda = 1.9115 \text{ \AA}$ ; 38, 86, 61. (c) Benzil,  $\lambda = 1.585 \text{ \AA}$ ; 13, 28, 59. (d) L-Ascorbic acid,  $\lambda = 1.632 \text{ \AA}$ ; 13, 27, 40.

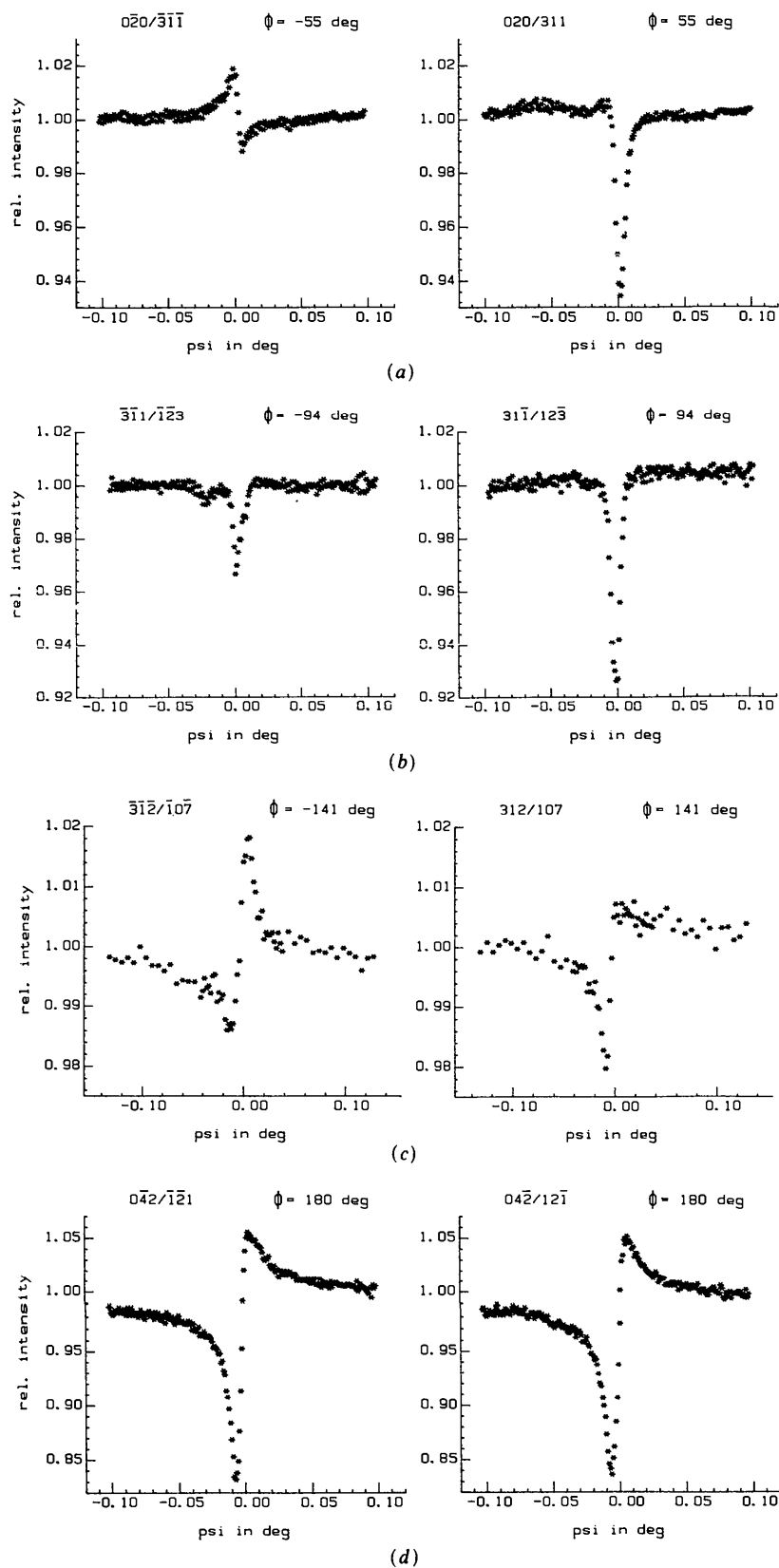


Fig. 5.  $\psi$ -scan profiles with *Aufhellung*. (a) L-Glutamic acid,  $\lambda = 2.0431$  Å; 17, 33, 33. (b) L-Glutamic acid,  $\lambda = 1.6700$  Å; 24, 24, 40. (c) Raffinose pentahydrate,  $\lambda = 1.8300$  Å; 39, 75, 55. (d) L-Glutamic acid,  $\lambda = 1.7610$  Å; 27, 54, 54.



phase near  $180^\circ$ . For this pair of profiles we would deduce a triplet phase of  $135^\circ$ ; however, the sign cannot be determined.

Such experimental uncertainties must be taken into account. The main reason is that the crystals are

orientated in different ways with respect to the incident beam when measuring the two centrosymmetric three-beam cases. The incident beam strikes different crystal faces. Fortunately, different asymmetric diffraction geometries do not influence the profiles very much, as we have checked by calculations.

It should be pointed out that the crystals need not be ideally perfect. Most of the crystals investigated show mosaicity, which can be seen in some three-beam profiles [cf. Figs. 3(b), 4(a) and 5(c)]. The mosaicity can be determined from the width of the two-beam profiles measured with a highly collimated incident beam. As a rule, if the FWHM of the two-beam profiles exceeds  $0.1^\circ$  with synchrotron radiation (divergence approximately  $0.01^\circ$ ), then the crystals cannot be used for multiple-beam experiments.

By visual evaluation 90% of about 300 triplet phases were determined correctly, i.e. 90% could be assigned to the correct octant. About 5% of the three-beam cases showed *Umweganregung* or *Aufhellung* effects so strongly that the error was greater than  $30^\circ$ . 5% of the profiles could not be used for phase determination; these profiles show irregularities incompatible with our catalogue.

This procedure of triplet phase determination was also tested with structures which were not yet solved at the time of the measurements, for example DIMA,

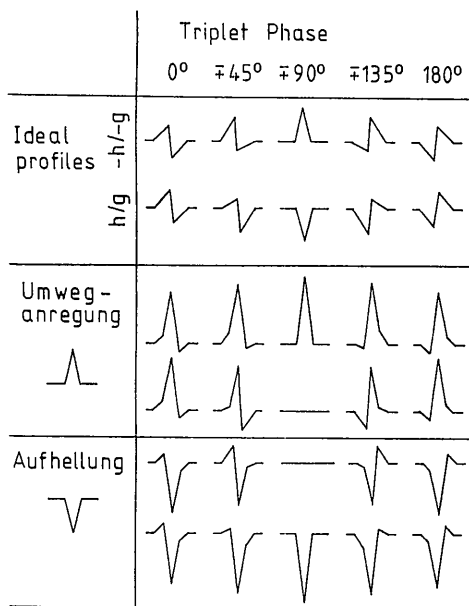


Fig. 6. Schematic drawings of observed three-beam  $\psi$ -scan profiles.

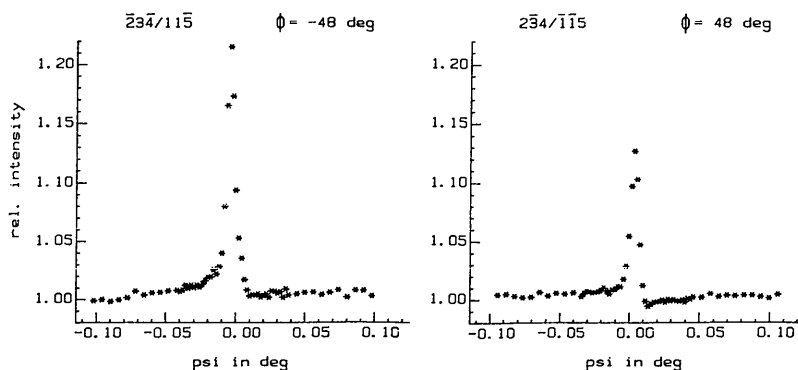


Fig. 7.  $\psi$ -scan profiles with strong *Umweganregung* leading to great errors in phase determination. Benzil,  $\lambda = 2.078 \text{ \AA}$ ; 9, 23, 25.

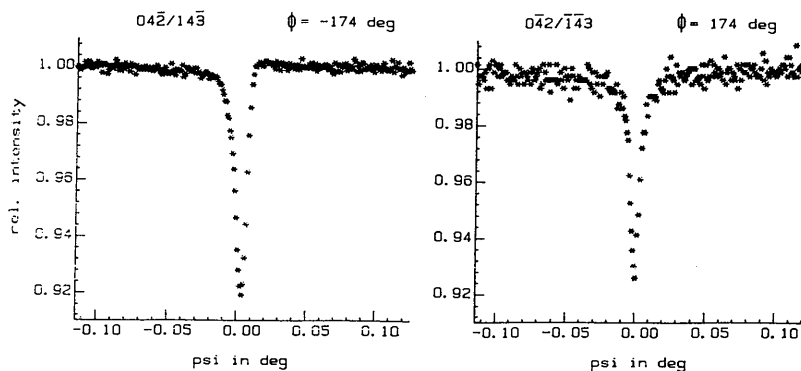


Fig. 8.  $\psi$ -scan profiles with strong *Aufhellung* leading to great errors in phase determination. L-Glutamic acid,  $\lambda = 1.922 \text{ \AA}$ ; 25, 10, 16.

propafenon and butafenon. Suitable three-beam cases with almost equal intensities of the reflections involved were selected from a data set measured prior to the three-beam measurements. The structures were later solved by direct methods.

There is one essential point open for further investigation. We have stated in the preceding theoretical paper (Weckert & Hümmer, 1990) that in Laue–Laue and Laue–Bragg diffraction geometry *Pendellösung* effects occur. Then the energy flow into the primary diffracted beam depends on the thickness of the crystal plate and the  $\psi$ -scan profiles with constant triplet phase depend on the crystal dimensions. By averaging over the *Pendellösung* the phase information is lost. Experimentally, we use non-cut crystals with grown faces, and the crystals are bathed by the incident beam. Therefore, the crystal thickness varies over the cross section of the diffracted beam. As a consequence, we guess that the *Pendellösung* effects are averaged out, so that the Laue–Laue and Laue–Bragg parts give no phase information. In addition, these are affected by anomalous absorption. Thus, we assume that only parts of the primary diffracted beam that are Bragg reflected carry the phase information.

In conclusion, the achievable accuracy of experimental triplet phase determination should be sufficient to solve structures that cannot be solved otherwise by a combination of measured triplet phases and direct methods.

These results were reported at the 11th European Crystallographic Meeting in Vienna (Weckert & Hümmer, 1988) and in part at the Fourteenth International Congress of Crystallography in Perth (Hüm-

mer, Bondza & Weckert, 1987; Weckert, Bondza & Hümmer, 1987).

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#### References

- BERMAN, H. M. (1970). *Acta Cryst.* **B26**, 290–299.  
 BROWN, C. J. & SADANAGA, R. (1965). *Acta Cryst.* **18**, 158–164.  
 BURZLAFF, H. (1988). Private communication.  
 HÜMMER, K. & BILLY, H. (1986). *Acta Cryst.* **A42**, 127–133.  
 HÜMMER, K., BONDZA, H. & WECKERT, E. (1987). *Acta Cryst.* **A43**, C222.  
 HÜMMER, K. & WECKERT, E. (1990). *Acta Cryst.* In the press.  
 HÜMMER, K., WECKERT, E. & BONDZA, H. (1989). *Acta Cryst.* **A45**, 182–187.  
 HVOSLEF, J. (1968). *Acta Cryst.* **B24**, 1431–1440.  
 KARTHA, G. & DE VRIES, A. (1961). *Nature (London)*, **192**, 862–863.  
 LEHMANN, M. S. & NUNES, A. C. (1980). *Acta Cryst.* **B36**, 1621–1625.  
 PAULUS, E. F. (1988). Private communication.  
 SHEN, Q. & COLELLA, R. (1988). *Acta Cryst.* **A44**, 17–21.  
 TANG, M. T. & CHANG, S. L. (1988). *Acta Cryst.* **A44**, 1073–1078.  
 WECKERT, E. (1990a). In preparation.  
 WECKERT, E. (1990b). In preparation.  
 WECKERT, E. (1990c). In preparation.  
 WECKERT, E., BONDZA, H. & HÜMMER, K. (1987). *Acta Cryst.* **A43**, C264.  
 WECKERT, E. & HÜMMER, K. (1988). *Z. Kristallogr.* **185**, 184.  
 WECKERT, E. & HÜMMER, K. (1990). *Acta Cryst.* **A46**, 387–393.

*Acta Cryst.* (1990). **A46**, 402–408

## Problems Associated with the Measurement of X-ray Attenuation Coefficients. II. Carbon Report on the International Union of Crystallography X-ray Attenuation Project

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#### Abstract

Measurements are reported of the mass attenuation coefficient of carbon taken by laboratories participating in the International Union of Crystallography

X-ray Attenuation Project. Data resulting from a similar study using silicon were published earlier [Creagh & Hubbell (1987). *Acta Cryst.* **A43**, 102–112]. The data are self consistent, for the most part, to 0.5% for the energy range 6 to 60 keV, and accords well