

which can be used for defective structures, so it should be possible to use these for relaxations or reconstructions, as well as features such as surface steps. Another approach which we intend to exploit in the near future is to employ the Bloch-wave solutions as the incoming wave for a multislice calculation which should allow us to calculate very accurately diffraction effects at surface steps, for instance. Limitations of the Bloch-wave approach aside, it does yield substantial physics, for instance the explanation of step spot splitting described in § 5.2.

References

- BETHE, H. A. (1928). *Ann. Phys. (Leipzig)*, **87**, 55-129.
 COLELLA, R. (1972). *Acta Cryst.* **A28**, 11-15.
 COLELLA, R. & MENADUE, J. F. (1972). *Acta Cryst.* **A28**, 16-22.
 COWLEY, J. M. (1981). *Diffraction Physics*. Amsterdam: North-Holland.
 FADDEEVA, V. N. (1959). *Computational Methods of Linear Algebra*. New York: Dover.
 HIRSCH, P. B., HOWIE, A., NICHOLSON, R. B., PASHLEY, D. W. & WHELAN, M. J. (1977). *Electron Microscopy of Thin Crystals*. London: Butterworths.
 HSU, T. & COWLEY, J. M. (1983). *Ultramicroscopy*, **11**, 239-250.
 ICHIMIYA, A., KAMBE, K. & LEHMPPFUHL, G. (1980). *J. Phys. Soc. Jpn.*, **46**, 684-688.
 KIKUCHI, S. & NAKAGAWA, S. (1933). *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **21**, 256-265.
 MA, Y. & MARKS, L. D. (1989). In preparation.
 MAKSYM, P. A. & BEEBY, J. L. (1981). *Surf. Sci.* **110**, 423-438.
 MARKS, L. D. & MA, Y. (1988a). *Acta Cryst.* **A44**, 392-393.
 MARKS, L. D. & MA, Y. (1988b). Submitted to *Surf. Sci.*
 MARTEN, H. & MEYER-EHMSEN, G. (1985). *Surf. Sci.* **151**, 570-584.
 MCRAE, E. G. (1966). *J. Chem. Phys.* **45**, 3258-3276.
 MCRAE, E. G. & CALDWELL, C. W. (1967). *Surf. Sci.* **7**, 41-67.
 MENADUE, J. F. (1972). *Acta Cryst.* **A28**, 1-11.
 METHERELL, A. J. (1972). *Electron Microscopy in Materials Science*, edited by U. VALDRE & E. RUEDL, Vol. II, pp. 397-552. Brussels: Commission of the European Communities.
 MIYAKE, S. & HAYAKAWA, K. (1970). *Acta Cryst.* **A26**, 60-70.
 MIYAKE, S., KOHRA, K. & TAKAGI, M. (1954). *Acta Cryst.* **7**, 393-401.
 MOON, A. R. (1972). *Z. Naturforsch. Teil A*, **27**, 390-395.
 PENG, L.-M. & COWLEY, J. M. (1986). *Acta Cryst.* **A42**, 545-552.
 PUKITE, P. R. & COHEN, P. I. (1987). *Appl. Phys. Lett.* **50**, 1739-1741.
 PUKITE, P. R., VAN HOVE, J. M. & COHEN, P. I. (1984). *Appl. Phys. Lett.* **44**, 456-458.
 SCHUMAN, H. (1977). *Ultramicroscopy*, **2**, 261-269.

Acta Cryst. (1989). **A45**, 182-187

Direct Determination of Triplet Phases and Enantiomorphs of Non-centrosymmetric Structures. II. Experimental Results

BY K. HÜMMER, E. WECKERT AND H. BONDZA

Institut für Angewandte Physik, Lehrstuhl für Kristallographie der Universität, Bismarckstrasse 10, D-8520 Erlangen, Federal Republic of Germany

(Received 19 April 1988; accepted 19 September 1988)

Dedicated to Ulrich Bonse on the occasion of his 60th birthday

Abstract

Direct measurements of triplet phase relationships for non-centrosymmetric light-atom organic structures with medium-size unit cells are reported. The phase information can be extracted from the three-beam profiles of a Renninger ψ -scan experiment. The measurements were carried out with a special ψ -circle diffractometer installed on a rotating Cu-anode generator. The incident-beam divergence is reduced to 0.02° . The experimental results confirm the theoretical considerations of paper I of this work [Hümmer & Billy (1986). *Acta Cryst.* **A42**, 127-133]. As triplet phases of $\pm 90^\circ$ can be distinguished, the absolute structure can be determined unambiguously. The measurements show that the triplet-phase-dependent interference effects may be superposed on phase-independent *Umweganregung* or *Aufhellung* effects. By a comparison of the ψ -scan profiles of two cen-

trosymmetrically related three-beam cases, the triplet phases of which have opposite signs, it is possible to evaluate the phase-independent effects and to determine the value of the triplet phase with an accuracy of at least 90° .

1. Introduction

In paper I of this work (Hümmer & Billy, 1986) the use of ψ -scan profiles near a three-beam case for the experimental determination of structure-invariant triplet phase sums was discussed in particular for non-centrosymmetric crystal structures. The idea of exploiting the three-beam interference to obtain information on the X-ray reflection phases is based on the fact that in an interference experiment the resultant amplitude depends not only on the amplitudes of the interfering waves but also on their phase difference (Lipscomb, 1949; Post, 1977).

From a kinematical point of view, in a three-beam case when the end points of two reciprocal-lattice vectors (r.l.v.) \mathbf{h} and \mathbf{g} lie simultaneously on or very near the Ewald sphere, the phase difference between the directly diffracted wave of \mathbf{h} (primary reflection) and the 'Umweg wave' generated by the scattering vectors \mathbf{g} and $\mathbf{h} - \mathbf{g}$, propagating in the same direction, is given by a triplet phase relationship:

$$\Phi = \varphi(-\mathbf{h}) + \varphi(\mathbf{g}) + \varphi(\mathbf{h} - \mathbf{g}).$$

The experimental procedure for systematically generating three-beam cases is the so-called ψ -scan or Renninger experiment. The crystal is rotated about the scattering vector \mathbf{h} which is in its reflection position and a second r.l.v. \mathbf{g} is scanned through the Ewald sphere.

As was shown in paper I, with the aid of the dynamical diffraction theory, scanning through the three-beam position, the amplitude of the 'Umweg wave' is continuously turned on and off and at the same time its phase is shifted by 180° with respect to the directly diffracted wave. This leads to characteristic ψ -scan profiles [intensity $I(\mathbf{h})$ as a function of ψ] near a three-beam position for triplet phases near $\Phi = 0, 180, \pm 90^\circ$. Accordingly, it should be possible to determine the value of the triplet phase sum from measured ψ -scan profiles with an accuracy of at least 90° . In addition the experimental discrimination of $\Phi = +90$ or -90° allows the determination of the absolute configuration or absolute structure (Jones, 1984). In this paper experimental results will be reported.

2. Experimental

A. The ψ -circle diffractometer

It is known that the angular width of the ψ -scan profiles is of the order of some arc minutes. Moreover, the intensity change due to the three-beam interference is only a few percent, when the structure factors involved have approximately the same magnitude. Therefore, the measurement of such ψ -scan profiles requires high precision in the angular resolution and in the ψ -scan accuracy of the diffractometer. In any case, one must avoid the case that the scattering vector of the basic reflection performs any staggering motion during the ψ scan, *i.e.* the scattering vector of the primary reflection must always lie exactly on the Ewald sphere, so it must not change its direction.

In our experimental experience exact ψ scans are difficult with a conventional four-circle diffractometer (see also Mo, Hauback & Thorkildsen, 1988). Therefore, a special ψ -scan diffractometer has been constructed (Fig. 1). This instrument contains two circles (θ, ν) for the detector with axes perpendicular to each other, and four circles for the crystal motion. The first crystal axis ω is parallel to the first detector axis ($\omega - 2\theta$ relation). Perpendicular to the ω axis a second

axis for the ψ rotation is installed. This ψ axis bears an Eulerian cradle with motions χ and φ . Thus an arbitrary scattering vector \mathbf{h} can be aligned with the ψ axis and a ψ scan is performed by moving only one circle. With the ν circle the detector can be moved above or below the horizontal plane defined by the incident beam and the ψ axis. In this way the ψ angle for the three-beam position can be controlled by measurement of the second Bragg reflection by means of a ψ scan.

All circles are driven by stepper motors which are computer controlled. The angular resolution of each axis is 0.001° .

B. X-ray equipment

The radiation source is a Rigaku rotating-anode generator operated at high brilliance, 12 kW mm^{-2} . It is equipped with a fine-focus gun assembly with an effective point focus of $0.1 \times 0.1 \text{ mm}$ on a copper anode. The maximum load was 1.2 kW at 50 kV . The copper radiation was filtered by a $100 \mu\text{m}$ nickel foil (β filter), hence the radiation spectrum used consists mainly of the $\text{Cu } K\alpha_1$ and $\text{Cu } K\alpha_2$ emission lines.

The divergence of the primary beam should be made as small as possible, consistent with keeping the counting rate of the basic reflection high enough. The divergence, determined by the size of the sample, by the effective focus size and by the crystal-to-focus distance (approximately 1 m) for our experiment, is 0.02° .

In order to reduce the absorption in air we placed a helium-filled tube between the radiation source and the crystal.

C. Crystals

As non-centrosymmetric test substances we chose organic structures without heavy atoms: (1) L-asparagine monohydrate, $\text{C}_4\text{H}_8\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$, space

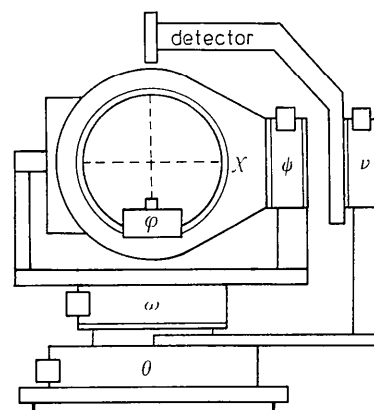


Fig. 1. Schematic drawing of the ψ -circle diffractometer. During the measurement of the three-beam ψ -scan profile the detector is set in the horizontal plane ($\nu = 0$ position).

group $P2_12_12_1$, cell parameters $a = 5.582$, $b = 9.812$, $c = 11.796$ Å, $Z = 4$, real and imaginary parts of $F(000)$: $F'(000) = \sum_j f_j + f_j' = 321$, $F''(000) = \sum_j f_j'' = 0.8$, linear absorption coefficient $\mu = 11$ cm $^{-1}$ for $\lambda = 1.54$ Å (Kantha & de Vries, 1961); (2) benzil, $C_{14}H_{10}O_2$, $P3_221$ or $P3_121$, $a = 8.376$, $c = 13.700$ Å, $Z = 3$, $F'(000) = 331$, $F''(000) = 0.57$, $\mu = 6.4$ cm $^{-1}$ for $\lambda = 1.54$ Å (Brown & Sadanaga, 1965).

The crystals were easily grown from solution by isothermal evaporation. The crystals used for the measurements were non-cut crystals; their cross section varied from 0.2 to 0.4 mm. The habit should be as nearly spherical as possible. As μt is always below 0.5, there should be no difference in the ψ -scan profiles for Bragg or Laue diffraction geometry (Hümmer & Billy, 1982).

D. Experimental procedure

The first step is to find a proper three-beam case for phase determination. This task has two aspects concerning the three-beam geometry and the structure-factor moduli. One has to realize that for Cu $K\alpha$ radiation the number of three-beam cases amounts to approximately 7000 for a unit-cell volume of about 650 Å 3 rotating the crystal by 360° about a scattering vector with $(\sin \theta)/\lambda = 0.17$ Å $^{-1}$ and taking into account that each r.l.v. g traverses the Ewald sphere twice; it enters (out-in case) and leaves (in-out case) the Ewald sphere or *vice versa*. It follows that the mean angular distance on the ψ scale between two three-beam settings is about 0.05°. Fortunately, the three-beam positions are not uniformly distributed on the ψ scale; there are regions of higher and lower density.

Given the cell parameters, the wavelength, and the orientation matrix, a computer program calculates the ψ angles of all multiple-beam positions for a selected basic reflection h . For the measurements we chose three-beam cases for which the angular distance to the adjacent multiple-beam position is greater than 0.1°.

The second criterion for selecting a certain three-beam case concerns the moduli of the structure factors involved. $F(h)$, $F(g)$ and $F(h-g)$ should be approximately of the same magnitude. This point will be discussed later in more detail.

The measuring time per step of the ψ -scan profile must be long enough to attain the required statistical precision. Generally, for a counting rate of the basic reflection of about 1000 counts s $^{-1}$, it takes several hours for one profile. During this time the two-beam intensity of the basic reflection h must be constant within 10 $^{-3}$. This condition can hardly be met. To avoid the influence of long-range intensity drift we use a multiple-scan technique.

The ψ -scan profile is obtained as the sum of several hundred very fast scans with a measuring time of

typically 0.5 s per step in each run. The total time at each measuring point is chosen so that the total number of counts per point is greater than 5×10^5 .

The measuring routines are computer controlled. First the scattering vector h is aligned with the ψ axis by a special centring routine. Then the profile of the h reflection is measured by means of an ω scan. The angular acceptance of the detector is so large that the detector can be fixed in the 2θ position. Next, the ω circle is positioned to the maximum of the h -reflection profile. At this ω position the profile of the second g reflection is measured by means of a ψ scan. For that, the detector must be positioned at the direction of the g reflection by motions in θ and ν . Thus the exact three-beam ψ position – the maximum of the g reflection – can be determined. Then the detector is moved back into the horizontal plane in which the h reflection appears and the ψ -scan profile is measured by scanning ψ about the three-beam position (see Figs. 2a,b).

3. Results and discussion

First of all we want to verify the theoretical results of paper I as far as the typical ψ -scan profiles near $\Phi = 0, 180, \pm 90^\circ$ are concerned. Secondly, ψ -scan profiles with *Aufhellung* (decrease) or *Umweganregung* (increase) effects are discussed with respect to their phase indication.

All the ψ -scan profiles were plotted in such a way that they represent an 'in-out' scan, *i.e.* the exact three-beam position is given by $\psi = 0$; for $\psi < 0$ the end point of g lies inside, for $\psi > 0$ it lies outside the

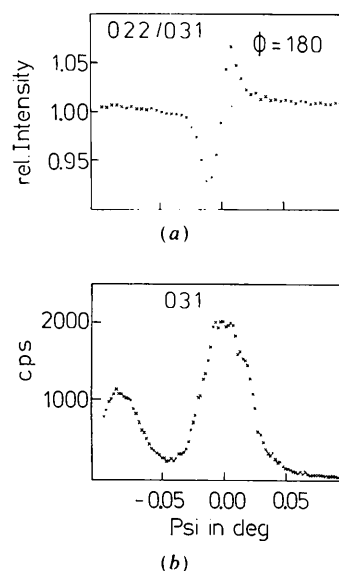


Fig. 2. (a) Three-beam ψ -scan profile for a triplet phase of 180° of L-asparagine: $F(022) = 17.2$, $F(031) = 29.1$, $F(0\bar{1}1) = 23.2$; $\varphi(022) = 180$, $\varphi(031) = 90$, $\varphi(0\bar{1}1) = -90$. (b) Profile of the 031 reflection by ψ scanning about the (022) scattering vector. The detector position is given by $\theta = 26.023$, $\nu = 11.457^\circ$. The ω position is that of the Bragg angle for (022): $\omega = 11.782^\circ$.

profile for $\Phi = 180^\circ$. No striking difference can be found on comparing the two profiles. Thus, obviously the *Umweganregung* effect is almost independent of the diffraction geometry, for the crystal is oriented differently to the incident beam in the case of h/g and $-h/-g$. In Figs. 6(a) and (b) an example of strong *Umweganregung* is shown. The *Umweganregung* overcompensates the attenuation due to the interference effect for $\Phi = 90^\circ$, i.e. the two-beam intensity is enhanced by about 5%. But for $\Phi = -90^\circ$

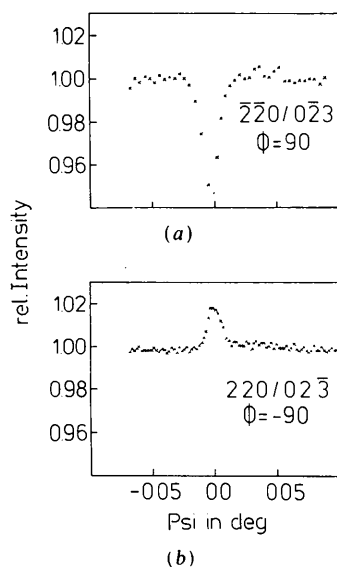


Fig. 4. Three-beam ψ -scan profiles with *Aufhellung* effect of L-asparagine. $F(\bar{2}20) = 23.8$, $F(0\bar{2}3) = 22.8$, $F(20\bar{3}) = 27.5$; $\varphi(220) = 0$, $\varphi(0\bar{2}3) = 180$, $\varphi(20\bar{3}) = -90^\circ$.

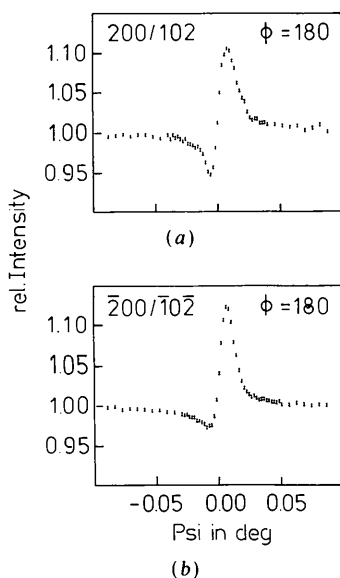


Fig. 5. Three-beam ψ -scan profiles with *Umweganregung* effect of L-asparagine. $F(200) = 15.4$, $F(10\bar{2}) = 25.1$, $F(10\bar{2}) = 25.1$; $\varphi(200) = 0$, $\varphi(10\bar{2}) = 180$, $\varphi(10\bar{2}) = 0^\circ$.

an increase of about 13% is measured. Thus, the phase-independent *Umweganregung* effect is approximately 9%, the interference effect is $\pm 4\%$. In spite of that, an unambiguous indication of the triplet phase can be deduced from the ψ -scan profiles.

The ψ -scan profiles of Figs. 6(a) and (b) were taken from single crystals of benzil. Benzil crystallizes in one of the enantiomorphous space groups $P3_121$ or $P3_221$. The phases indicated in the diagrams are calculated from the structure data consistent with $P3_221$ and they coincide with the phases deduced from the ψ -scan profiles. In principle, with this single measurement the absolute configuration of the structure can be determined. We investigated benzil mainly with synchrotron radiation. The results will be reported in another paper.

4. Concluding remarks

In paper I we discussed the interference effect near a three-beam position by means of a modified two-beam approximation (Bethe approximation). We have only considered the influence of the *Umweganregung* wave on the directly diffracted wave. We have not considered the fact that each beam scatters into the other beams and we have not taken into account any boundary conditions. Therefore, no *Aufhellung* effects can be predicted.

Moon & Shull (1964) calculated the intensity change in a multiple-beam diffraction case by means of a coupled set of differential equations which have the conservation of energy as one of the fundamental hypotheses. Each beam is depleted by scattering into the other beams and enhanced by scattering from the

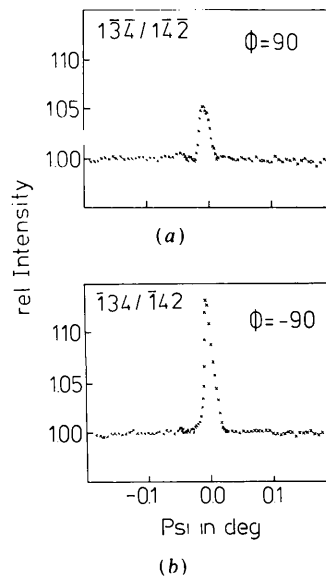


Fig. 6. Three-beam ψ -scan profiles with strong *Umweganregung* effect of benzil. $F(1\bar{3}4) = 17.2$, $F(1\bar{4}2) = 29.9$, $F(01\bar{2}) = 42.0$; $\varphi(\bar{1}34) = -87$, $\varphi(\bar{1}42) = -63$, $\varphi(01\bar{2}) = -120^\circ$.

other beams into itself. In summary, the intensity change of the primary reflection caused by the presence of at least one secondary reflection can be either positive (*Umweganregung*) or negative (*Aufhellung*) independent of the phase relationships between the different reflections. It depends only on the structure-factor moduli. Thus, in a three-beam case these effects are independent of the triplet phase and we denote them as phase independent. Moon & Shull (1964) pointed out that in the limit of low extinction and weak absorption the intensity change is independent of the diffraction geometry, *i.e.* the diffracted beams can be of either transmission (Laue) or reflection (Bragg) type or any mixture thereof.

On the other hand it was shown by dynamical-theory calculations (Hümmel & Billy, 1982) that in the limit of weak absorption ($\mu t < 0.5$) the three-beam interference effect is also independent of the diffraction geometry. This criterion was always fulfilled. In our experiments both the interference effects and the phase-independent *Umweganregung* and *Aufhellung* effects are independent of the diffraction geometry, as can be seen in Figs. 5(a) and (b), where the couple of centrosymmetric three-beam cases have the same triplet phase. No significant differences of the profiles can be found.

The experimental results show that in general there is a superposition of the phase-independent and interference effects. The phase-independent effects may predominate over the interference effects if the ratio of the intensities of the primary reflection $I(\mathbf{h})$ and the secondary reflection $I(\mathbf{g})$ is too low or too high. In these cases it is very difficult to deduce any phase information from the ψ -scan profiles and to distinguish $+90^\circ$ and -90° profiles.

It should be pointed out that the discrimination of triplet phases near $\pm 90^\circ$ by the experiment allows the

determination of the absolute configuration of a non-centrosymmetric structure or the determination of the absolute structure (Jones, 1984) because two enantiomorphic structures differ in the signs of the triplet phases. In this connection it should be mentioned that on the basis of a right-handed system of coordinates it is always possible to index all reflections without knowledge of the absolute structure. Here we do not agree with Shen & Collella (1986). In the case of benzil, for example, assuming atomic parameters consistent with the space group $P3_121$ would be in contradiction to the signs of the triplet phases determined from the experiment. Therefore, for our crystals $P3_221$ is the correct space group and the absolute configuration is given by the set of atomic coordinates consistent with this space group.

For L-asparagine the coordinates of Kartha & de Vries (1961) are confirmed.

The authors thank Professor H. Burzlaff. The ψ -circle diffractometer was built according to his proposal. This work was supported by the Deutsche Forschungsgemeinschaft.

References

- BROWN, C. J. & SADANAGA, R. (1965). *Acta Cryst.* **18**, 158–164.
 HÜMMER, K. & BILLY, H. (1982). *Acta Cryst.* **A38**, 841–848.
 HÜMMER, K. & BILLY, H. (1986). *Acta Cryst.* **A42**, 127–133.
 JONES, P. G. (1984). *Acta Cryst.* **A40**, 660–662.
 KARTHA, G. & DE VRIES, A. (1961). *Nature (London)*, **192**, 862–863.
 LIPSCOMB, W. N. (1949). *Acta Cryst.* **2**, 193–194.
 MO, F., HAUBACK, B. C. & THORKILDSEN, G. (1988). *Acta Chem. Scand. Ser. A*, **42**, 130–138.
 MOON, R. M. & SHULL, C. G. (1964). *Acta Cryst.* **17**, 805–812.
 POST, B. (1977). *Phys. Rev. Lett.* **39**, 760–763.
 SHEN, Q. & COLLELLA, R. (1986). *Acta Cryst.* **A42**, 533–538.

Acta Cryst. (1989). **A45**, 187–193

Crystallography, Geometry and Physics in Higher Dimensions.

V. Polar and Mono-Incommensurate Point Groups in the Four-Dimensional Space \mathbb{E}^4

BY R. VEYSSEYRE AND D. WEIGEL

Laboratoire de Chimie-Physique du Solide (Unité Associée au CNRS no. 453) et Laboratoire de Mathématiques de la Physique, Ecole Centrale des Arts et Manufactures, Grande Voie des Vignes, 92295 Châtenay-Malabry CEDEX, France

(Received 4 May 1988; accepted 21 September 1988)

Abstract

The crystallographic point groups of the four-dimensional Euclidean space \mathbb{E}^4 are a convenient means of studying some crystallized solids of physical space, for instance the groups of magnetic structures

and the groups of mono-incommensurate structures, as is demonstrated by a simple example. The concept of polar crystallographic point groups defined here in \mathbb{E}^4 , and also in \mathbb{E}^n enables the list and the WPV notation {geometric symbol of Weigel, Phan & Veyseyre [*Acta Cryst.* (1987), **A43**, 294–304]} of these