New Features in EXPO2007, a Program for Crystal Structure Resolution from Powder Data

Angela Altomare,[a] Corrado Cuocci,[b] Carmelo Giacovazzo,[a,b,*] Anna Moliterni,[a] and Rosanna Rizzi[a]

[a]*Istituto di Cristallografia, Sede di Bari, Via G. Amendola 122/o, 70126 Bari, Italy*

[b]*Dipartimento Geomineralogico, Università di Bari, Campus Universitario, Via Orabona 4, 70125 Bari, Italy*

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New approaches have been introduced in the EXPO2007 program aiming at making easier and straightforward the *ab initio* crystal structure solution from powder diffraction data. Improvements in space group determination, powder pattern decomposition, least squares Fourier recycling, interpretation of the electron density map have been developed. To manage organic crystal structures a new strategy in direct-space, combining Direct Methods and Simulated Annealing approaches, has been implemented.

INTRODUCTION

In the last years the interest for the *ab initio* crystal structure solution by powder diffraction data has considerably increased. A great number of experimental and theoretical efforts have been made to reduce the effects of peaks overlapping, to correct background estimation and preferred orientation. Home diffractometers, and particularly, synchrotron sources, are now able to provide high quality experimental patterns which, combined with new powerful computing procedures, have made possible the solution of a large number of crystal structures. Two main approaches can be used for solving crystal structures by powder data: real-space strategies and two-stage methods. The first one, may be applied only when some prior information on the molecular geometry is available; it uses: Monte Carlo,[1,2] Genetic Algorithm,[3–5] Simulated Annealing[2,6–9] or parallel tempering[10] approaches and is particularly able to manage organic structures.

Today organic compounds with a large number of non-hydrogen atoms in the asymmetric unit and with large number of degrees of freedom (used to describe the molecular model) can be routinely solved. The two-stage approach (working in reciprocal space) performs first the extraction of the integrated intensities from the experimental powder pattern then Direct Methods[11] are applied to assign phases values to a sufficiently large number of reflections from where the electron density maps may be calculated. This is the preferred choice when only the experimental pattern and the unit cell content are available. EXPO2004 (Ref 12) is a two-stage method based program; in case of prior information on the molecular geometry real space strategies can be also used.

Recently the program has been endowed with new routines aiming at making more straightforward the *ab initio* crystal structure solution. The main steps of this new version of EXPO2004 (said EXPO2007) are:

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* Author to whom correspondence should be addressed. (E-mail: carmelo.giacovazzo@ic.cnr.it)

a) indexation, performed by N-TREOR,[13] a revised and strengthened version of TREOR program.[14] The procedure is able to automatically take several decisions and to manage data with $2\theta_o$-shift error;

b) extraction of integrated intensities by powder pattern decomposition using the Le Bail method.[15] To improve its potentiality, the method can be combined with additional information coming out from electron density or Patterson methods;[16–20]

c) space group determination process, based on a probabilistic approach taking into account reflection overlapping;[21–23]

d) Direct Methods application for phasing reflections and providing electron density maps;

e) Rietveld refinement;[24]

f) global optimization methods,[25] when organic structures are investigated and information about the molecular geometry is available.

EXPO2007 has also been modified for treating protein powder data with respect to the steps a)–c). We describe here some new aspects of the program.

SPACE GROUP DETERMINATION

Unlike for single crystal diffraction data, the determination of the extinction symbol (ES) may be a complicate task for powder data. This is related to the uncertainty in the background estimation, to the presence of textures and to the overlapping of the diffraction peaks. This is the reason why an inspection of the observed diffraction pattern is the largely used approach to space group determination. Some new algorithms have been developed by Altomare *et al.*,[21–23] and implemented in the EXPO2007 program. The procedure is based on the statistical analysis of the normalized $|E|^2$ intensities as extracted by the experimental powder pattern in the space group having the largest Laue symmetry compatible with the assumed crystal system (and no extinction conditions). The extracted intensities are normalized according to the Wilson statistics, and the $|E|^2$-statistics, is used to define each probability of each extinction symbol $P(ES)$ by using appropriate weights for single and for overlapping reflections. At the end of the procedure the program gives a list of possible extinction symbols ordered according to $P(ES)$. When pseudotranslational symmetry is present the most probable ES does not always coincide with the true one. In this case $P(ES)$ is a rather flat figure of merit and the direct user inspection of the experimental diffraction pattern is frequently necessary to eliminate false ES indications.

To make the identification of the correct ES as automatic as possible, the procedure was integrated with two new algorithms:[23] 1) the compilation of a control peak list, containing a subset of weakly overlapping reflec-

TABLE I. For each test structure we give: the code name, the correct extinction symbol (cES), the order number (orn) at which it is ranked by the space group determination procedure according to EXPO2004 and EXPO2007

Codename	cES	EXPO2004	EXPO2007
		orn	orn
BAMO	$P\ 1\ 2_1\ 1$	3	2
NICKEL	$P\ 1\ 2/c\ 1$	2	2
ZOPI	$P\ 1\ 2_1/c\ 1$	12	3
YONO	$P\ 1\ 2_1\ 1$	2	2
AGPZ	$P\ b\ c\ a$	25	7
CFCL	$F\ d\ d\ \_$	1	2
RUCO	$I\ b\ a\ \_$	2	2
SALBU	$P\ b\ c\ a$	2	2
SCAMPHOR1	$P\ 2_1\ 2_1\ 2_1$	5	6
SODIUM	$P\ b\ c\ n$	41	3
SRRU	$P\ n\ m\ a$	71	2
VNI	$P\ 4_1\ 2_1\ \_$	24	12
F1A	$R\ \_\ \_$	7	7
VFI	$P\ 6_3\ \_\ \_$	2	2

tions, to check if some of them violate the extinction rules of the chosen ES; 2) the identification of low intensity 2θ intervals in the powder pattern to identify the regions of the experimental pattern where the $|E|^2$-intensities are wrongly estimated.

The complete procedure, implemented in EXPO2007, was tested on 75 structures. For 61 of them the procedure is able to find the correct extinction symbol in the first position in the $P(ES)$ list. For the rest, we quote in Table I a comparison with the results obtained by the standard EXPO2004 procedure.

LEAST-SQUARES FOURIER RECYCLING

In any procedure for *ab initio* crystal structure solution the last step is the completion and refinement of the structural model, independently if it is obtained using real-space approaches or Direct/Patterson methods. Historically the Rietveld method is used to complete and refine powder data making a least-squares minimization of:

$$S = \sum_i w_i \left| y_{io} - y_{ic} \right|^2 \qquad (1)$$

where w_i is a suitable weight, y_{io} and y_{ic} are the observed an calculated intensities respectively. In this case the parameters to be refined are the unit cell, the atomic positions, the thermal parameters and the variables related to the peak shape function and background. Owing to the strong correlation among the various parameters and when the model to refine is approximated, the method results slowly convergent. An alternative is to minimize the residual:

TABLE II. For each test structure: CODE is the code name; for the *ith* atomic species AS(i), NA(i) is the number of (non-hydrogen in case of X-rays) atoms to locate in the asymmetric unit; NAT$_{DM}$ is the number of symmetry independent atoms close to the published atomic co-ordinates (with a distance less that 0.6 Å) as found in the first electron density map calculated just after the Direct Methods (DM) step; $<d>_{DM}$ is the average distance of the NAT$_{DM}$ peaks from the corresponding atoms in the published crystal structure; NAT$_{ref}$ is the number of atoms close (with a distance less that 0.6 Å) to the published atomic coordinates at the end of the EXPO2007 refinement step. $<d>_{ref}$ is the average distance of the NAT$_{ref}$ peaks from the corresponding atoms in the published crystal structure.

CODE	AS(i), NA(i)	NAT$_{DM}$	$<d>_{DM}$	NAT$_{ref}$	$<d>_{ref}$
AGPZ	Ag1N2 C3	3	0.474	4	0.418
AND1	O2 N5 C7	14	0.131	14	0.084
AND2	O5 N6 C6	17	0.131	17	0.143
BACO	Ba1 C1 O3 H1	5	0.105	6	0.039
BAMO	Ba2 Mo6 O20	20	0.317	28	0.235
BENZ	F3 C6	9	0.107	9	0.059
CAPTO	S1 O3 N1 C9	9	0.289	12	0.312
CF3BR	Br1 F3 C1	5	0.075	5	0.024
CLOMIPRA	Cl2 N2 C19	14	0.348	20	0.319
CIME	S1 N6 C10	17	0.090	17	0.074
CROX	Cr4 O11	14	0.242	15	0.191
CUPZ	Cu1 N2 C3	3	0.411	6	0.182
DADA	Ti1 K2 Si3 O10	8	0.271	14	0.165
FAMO	S3 O2 N7 C8	19	0.103	20	0.091
GAPO	Ga4 P4 F1 O16 C7	13	0.297	20	0.319
LAMO	La1 Mo5 O8	11	0.265	13	0.165
LEFEBVRE	N2 C14	15	0.189	16	0.154
NBPO	Nb3 P4 O15	21	0.201	22	0.062
NICKEL	Ni1 Cl1 P1 C18	5	0.369	21	0.197
NIZR	Zr2 Ni1 P3 O12	8	0.352	16	0.259
PBS	Pb1 S2 O3	3	0.148	4	0.179
SBPO	Sb2 P3 O12	9	0.282	11	0.290
SGT	Si4 O7 C6	13	0.071	12	0.106
SULPH	S2 D3	5	0.065	5	0.022
UTM1	Si6 O13	18	0.163	19	0.138
YONO	Y4 O13 N1	15	0.202	16	0.225

$$R = \sum_h w_h (I_{oh} - I_{ch})^2 \qquad (2)$$

where w_h is a suitable weight, I_{oh} and I_{ch} are the integrated intensity extracted from the experimental pattern and calculated by the model respectively. The summation is over all the reflections in the pattern. When powder data are managed, the use of Eq. (2) may be questionable in several cases owing to the collapse of the three-dimensional reciprocal space onto the 2θ axis. In EXPO2007 the model optimization is based on the least squares minimization of the residual in Eq. (2), in which a new sensible weighting scheme has been implemented:[26]

$$w_h = w_{1h} \cdot w_{2h}$$

$$w_{1h} = w_{ah} \cdot w_{bh} \qquad w_{2h} = 1 / [1 + 4 \cdot (m_h \cdot L_h \cdot |F_{oh}|)^2]$$

$$w_{ah} = \exp[-0.5 \cdot (\sin\theta_h / \lambda)^2] \qquad w_{bh} = \sqrt{I_{oh} / I'_{oh}}$$

where for the h reflection, m_h is its multeplicity, L_h the Lorentz-polarization factor, $|F_{oh}|^2 = (I_{oh}/m_h L_h)$, θ_h the angular position, λ the wavelength radiation, $I_{oh} = \sum_k (1 - q_{kh}^2) I_{ok}$ and $q_{kh} = |2\vartheta_k - 2\vartheta_h| / \text{FWHM}_h$, FWHM_h the full width at half maximum of the reflection peak.

w_{1h} decreases with increasing θ_h values (it is more difficult to carefully model overlapping and background in the high angle region of the experimental pattern), where the number of reflections in overlapping is large. w_{2h} is the typical weight used for powder data to avoid that least squares are dominated by the largest intensities. The parameters under refinement are the crystallographic fractional coordinates and the isotropic thermal factor of any symmetry independent atom. The new procedure, completely automatic, is able to considerably improve the structural model supplied by Direct Methods and therefore provides a better model for the final Rietveld refinement (see Table II).
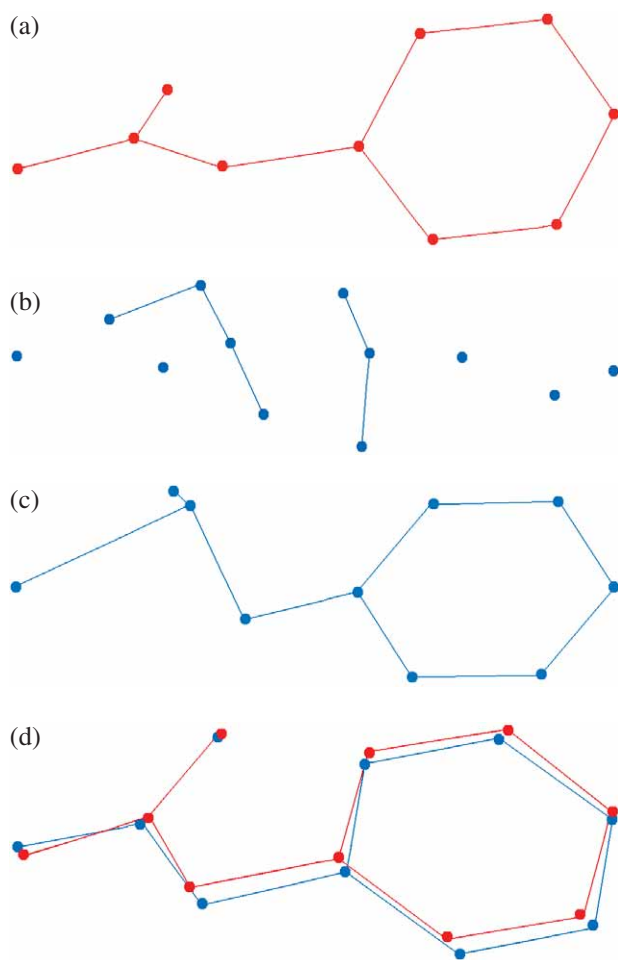
(a)

(b)

(c)

(d)

Figure1a-1d. Structure models of PHENYLA according to the various steps of the procedure (see main text).

COMPLETION OF THE ELECTRON DENSITY MAP

At the end of a standard Direct Methods procedure an electron density map is produced that, especially for organic compounds, is usually very approximate and hardly interpretable: some atoms are imperfectly located, others are in completely wrong positions and some atoms are missing. In these cases the connectivity of the structure is quite low and scarcely informative. In EXPO2007 a new procedure was implemented[27] aiming at recovering the full information contained in the electron density map and leading to the crystal structure solution. The only information necessary to apply the procedure is the knowledge of the molecular geometry. The algorithm performs the following steps:

1) Automatic interpretation of Direct Methods electron density map like in EXPO2004;

2) Discarding false atomic positions. The operation is performed *via* a suitable combination of two figures of merit:

$$\chi = \Sigma w_I (I_o - I_c)^2 \quad \text{and} \quad R = \Sigma w_y (y_o - y_c)^2 \quad (3)$$

w_I is a suitable weight, I_o and I_c are the intensities extracted from the experimental pattern and calculated by the current model respectively. $w_y = 1/y_o$, y_o and y_c are the observed and the calculated counts respectively. The atom for which the ratio $(\chi_i R_i) / (\chi_{DM} R_{DM})$ is a minimum is eliminated and the model is updated. χ_{DM}, R_{DM} and χ_i, R_i are the quantities calculated using the model obtained just after the application of Direct Methods and after the elimination of the *ith* atom of the molecular model respectively. The procedure is repeated until no atom is discarded.

3) Recovering the missing atoms. The missing positions are built one at a time by geometrical construction, by using the expected values of distances and angles.

4) Improving the atomic positions. Cycles of least-squares are performed to automatically optimize the molecular model. Restraints on bonds and angles are applied allowing the procedure to be effective.

We describe the application of the new approach with an example.

PHENYLA structure,[28] space group *P* 21/a, unit cell content $C_{32}H_{60}N_4O_{12}S_4$, $Z = 4$ and experimental resolution equal to 1.43 Å. The true molecular model is shown in Figure 1a. A default run of EXPO2004 gives an electron density map which, interpreted by standard tools, provides the model in Figure 1b. Such model is uninterpretable, the atoms are scarcely connected, but 8 of the 12 peaks are at a distance less than 0.6 Å from the correct atomic positions, with average distance $<d> = 0.30$ Å and overall phase error $<\Delta\varphi> = 52°$ for the 258 reflections in the measured 2θ range. The above data suggests that some structural information is present in the map, but as consequence of the errors on the extracted integrated intensities, of the limited data resolution and of the effect of the phase error, no chemically interpretable model can be obtained from the Fourier syntheses. After the execution of steps 1–3 the resultant model is given in Figure 1c. Nine of the ten atoms are close to the true ones with $<d> = 0.32$ Å. The overall phase error is $<\Delta\varphi> = 32°$. The structural model obtained at this step is optimized performing cycles of least squares minimizing the first figure of merit in the Eq. (3). The final refined structure (in blue), compared with the true model (in red), is shown in Figure 1d.

DIRECT SPACE APPROACHES

Direct Methods frequently fail when applied to molecules without heavy atoms or with a low experimental data resolution. At the contrary real-space techniques are less demanding for the quality of diffraction data, because they use a supplementary information (when available): the molecular geometry. The principal limita-
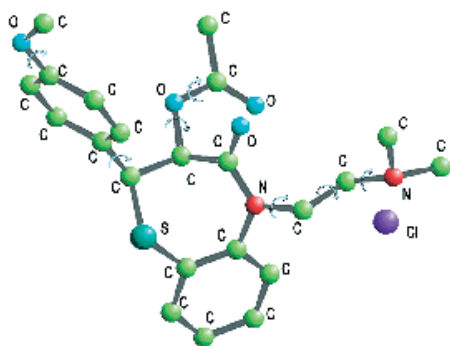
Figure 2. Molecular model of DILTIA structure. The torsion angles considered as internal degrees of freedom are indicated by arrows.

tion is related to the number of degrees of freedom necessary to describe the molecule. A combination of Direct Methods and Simulated Annealing technique has been implemented in EXPO2007.[25] The idea is to exploit the potentiality of both methods by combining the information present in the electron density map produced by Direct Methods with an approximate molecular model in the parameters space by using Simulated Annealing as global optimization method.[29] In the procedure the trial model is described in terms of internal coordinates, *i.e.,* bond lengths, bond angles and torsion angles as free parameters. In our procedure the position of the model is kept fixed because the algorithm associates progressively each peak of the Fourier map to each atom of the model. The quality of each trial configuration is described by a cost function (CF):

$$CF = \frac{\sum |I_{oss} - KI_{calc}|}{\sum I_{oss}} \qquad (4)$$

where $I_{oss} = |F_{oss}|^2$ is the observed intensity (*i.e.,* as estimated by Le Bail method), I_{calc} is the intensity calculated from the trial model and K is a scale factor. The reflections involved in Eq. (4) are selected among the low resolution structure factors, and they are single or in clusters of two overlapping reflections. The Metropolis criterion[30] is used to reject or accept a trial configuration; if the model is accepted, it is submitted to a local minimization.

At the end of the procedure, the list containing the best models is submitted to a weighted least-squares refinement. In order to avoid that the connectivity of the molecular model breaks in the successive cycles, bond distances and angles are automatically restrained to their expected values. The procedure has been applied with success to a large number of organic structures; as an example we quote the case of DILTIA:[28] at the end of the Direct Methods step, EXPO2007 generates an electron density map from which the highest six peaks are selected and used as pivots of the Simulated Annealing procedure. They are all isolated (*i.e.,* not at bond distance from any other peak) and sufficiently close to their published atomic positions, with an average distance $<d> = 0.50$ Å. The experimental data resolution is equal to 2.18 Å. The flexibility of the molecule model may be described by seven torsion angles showed in Figure 2. In addition a chlorine atom is expected to be in the solvent region, isolated from to the rest of the molecule, so leading to 15 the total number of degrees of freedom. The highest peak of the Fourier map is assumed to be coincide with the Cl position: this allows to spare 6 degrees of freedom in the search. In 228 minutes, using a LINUX Intel Xeon of 3.06 GHz, all the procedure is ex-

TABLE III. For each test structure: CODE is the code name; CELL indicates the published cell parameters; SG is the published space group; N-TREOR RANK is the rank of the correct cell among the plausible unit cells, listed in function of the M'_{20} figure of merit; orn is the order number of the correct extinction symbol as supplied by EXPO2007

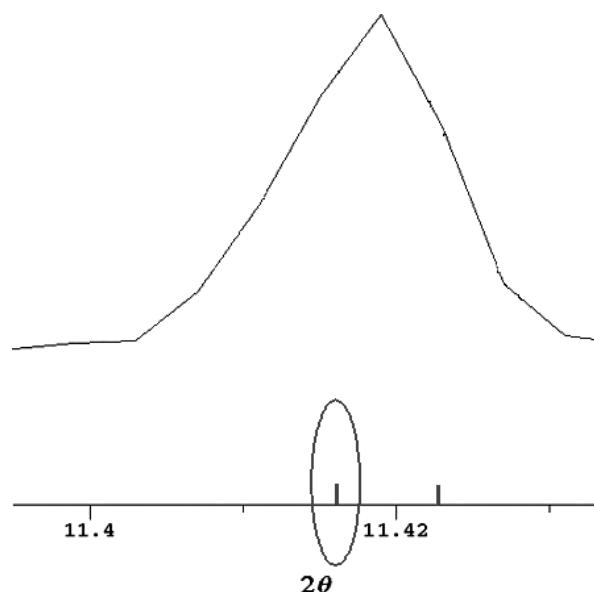| CODE	CELL	SG	N-TREOR RANK	orn
APOFERRITIN	$a = 184.305 = b = c$ $\alpha = \beta = \gamma = 90.0\,°$	$F432$	1	1
HEWL	$a = 78.844 = b, c = 38.188$ $\alpha = \beta = \gamma = 90.0\,°$	$P4_32_12$	1	1
CUBIC INSULIN	$a = 79.001 = b = c$ $\alpha = \beta = \gamma = 90.0\,°$	$I2_13$	2	1
HEXAGONAL INSULIN	$a = 82.495 = b, c = 33.650$ $\alpha = \beta = 90.0\,°, \gamma = 120.0\,°$	$R3$	1	6
TEWL	$a = 71.198 = b, c = 85.205$ $\alpha = \beta = 90.0\,°, \gamma = 120.0\,°$	$P6_122$	1	1
THAUMATIN	$a = 58.731 = b, c = 151.614$ $\alpha = \beta = \gamma = 90.0\,°$	$P4_122$	1	1

Figure 3. HEXAGONAL INSULIN: experimental profile (black line) and calculated reflection positions (red vertical bars) around $2\theta = 11.42°$. The position of reflection ($10 - 3\ 3$) satisfying the R condition is marked by an ellipse.

ecuted and all the atoms in the asymmetric unit (30) are found close to the published atomic coordinates with an average distance $<d> = 0.13$ Å.

POWDER DIFFRACTION DATA BY PROTEINS: FIRST APPLICATIONS OF EXPO2007

In the last years, high-resolution synchrotron X-ray powder diffraction has been successfully exploited for characterizing and refining small proteins.[31–35] The new and recently increased interest in protein powder crystallography encouraged the optimization of EXPO2007 for treating diffraction data by proteins, automatically performing the steps of indexation, powder pattern decomposition and space group determination.

TABLE IV. HEXAGONAL INSULIN: ten extinction symbols ES in order of P(ES).

ES	P(ES)
$P6_2$ _ _	0.770
$P3_1$ _ _	0.770
$P6_1$ _ _	0.703
$P6_3$ _ _	0.549
P _ _ _	0.086
R(obs)_ _	0.042
R(rev)_ _	0.042
P _ _ c	0.014
P _ c_	0.002
R(obs)_ c	0.001

EXPO2007 has been applied to a set of test structures whose main crystallographic data are supplied in Table III. For most proteins the first ranked solution (*i.e.* the cell parameters or the extinction group) is the correct one (see Table III), except for two cases (CUBIC INSULIN[36] for the indexation and HEXAGONAL INSULIN[36] for the space group determination) that we briefly discuss.

Cubic Insulin

At the end of the indexation step the most plausible cells were ranked by N-TREOR in function of the M'_{20} (Ref. 13) figure of merit. The two highest figures of merit M_{20} (Ref. 37) and M'_{20} (Ref. 13) correspond to:

1) $a = 55.8494$ Å, $c = 39.4743$, tetragonal system, $M_{20} = 132$, $M'_{20} = 660$, number of unindexed lines (NIX) = 0;

2) $a = 78.9716$ Å, cubic system, $M_{20} = 76$, $M'_{20} = 456$, NIX = 0. This cell has a volume four times higher than the tetragonal one, respectively (see Table III). However the correct cubic cell should be preferred if considerations on the expected volume are used.

Hexagonal Insulin

The correct space group of the hexagonal Insulin is $R3$. In Table IV we show the first ten extinction groups ES in order of the probability P(ES), as calculated by EXPO2007 by using the cell parameters suggested by N-TREOR. The right ES is erroneously located at 6 in the list (see Table III); the main reason is due to errors in the reflection intensity estimates. *I.e.*, some of reflections with Miller indices satisfying the 'R condition' ($-h + k + l \neq 3n$, where n is an integer), show non vanishing intensities. An example [reflection ($10 - 3\ 3$)] is shown in Figure 3: the overlapping is the main reason of the wrong intensity estimates. Indeed the Le Bail decomposition procedure assigns $z = 5.153$ to the reflection ($10 - 3\ 3$) while it should be absent ($z = 0.0$). This problem is related to the quality and reliability of the full pattern decomposition step that, in case of proteins, can be very critical, owing to reflections overlapping.

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SAŽETAK

Nove značajke u EXPO2007, programu za rješavanje kristalne structure iz podataka praha

Angela Altomare, Corrado Cuocci, Carmelo Giacovazzo, Anna Moliterni i Rosanna Rizzia

Uvedeni su novi pristupi u programu EXPO2007 koji olakšavaju i pojednostavljuju *ab initio* određivanje kristalne strukture iz difrakcijske slike kristalnog praha. Razvijena su poboljšanja u određivanju prostorne grupe, razlaganju difrakcijske slike praha, utočnjavanju kristalne strukture Fourierovom analizom i interpretaciji raspodjele elektronske gustoće. Nova strategija u kristalnom prostoru, a koja predstavlja kombinaciju direktnih metoda i pristupa simuliranog oporavka (simulated annealing) rešetke primjenjena je u određivanju kristalnih struktura organskih spojeva.