When a crystal surface is deformed, the standing waves can only be assumed to be hooked to the perfect bulk lattice planes for the first ten or so atomic layers at any angle of incidence, but are hooked throughout the whole thickness at the exact Bragg angle for the substrate. In all other cases the node spacing depth distribution is different from either that of the bulk or that of the deformed crystal. Great caution should therefore be taken in interpreting standing-wave results of crystals with a deformed surface layer or an overlayer with a slightly different lattice parameter.

If, however, an appropriate elastic model describing the strain distribution in the deformed crystal is known, the exact position of the nodes can be deduced from the phase distribution $\psi(\eta, z)$ and the standing-wave field calculated. By comparing the results with experimental measurements it is then possible to determine atom location at the surface or inside the deformed layer, as in the perfect-crystal case. The amount of strain in the epilayer of a heterostructure can be determined as has been shown by Koval'chuk *et al.* (1987) and the steepness of the interface estimated.

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SHORT COMMUNICATIONS

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Direct methods and structures showing superstructure effects. V. The use of one-phase seminvariants and quartet invariants.

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Abstract

Figures of merit based on PSI0 and on strong triplets are often unreliable for structures with superstructure effects. Prior information on pseudotranslational symmetry is used in order to estimate one-phase seminvariants. These are used, together with quartet invariants, for finding the correct solution in a multisolution process.

Symbols and abbreviations

Papers by Cascarano, Giacovazzo & Luić (1988*a*, *b*) will be denoted respectively as papers III and IV.
s.s.: structure seminvariant.
s.i.: structure invariant.
Other symbols as in paper III.

Introduction

Different probabilistic approaches are today available for estimating triplet invariants in crystal structures with superstructure effects (Böhme, 1982, 1983; Fan Hai-fu, Yao Jiaxing, Main & Woolfson, 1983; Gramlich, 1984; Cascarano, Giacovazzo & Luić, 1985, 1987, 1988*a*, *b*). No attempt has so far been made for estimating (in a probabilistic sense) other types of s.i.'s or s.s.'s, even if their role in this kind of structure is expected to be non-negligible.

Default runs of the *SIR* package (Cascarano, Giacovazzo, Burla, Nunzi, Polidori, Camalli, Spagna & Viterbo, 1985) involve, besides triplets, also quartet invariants and one- and two-phase seminvariants. However, only triplets are used for structures with superstructure effects according to papers III and IV. Even if they are successful in solving such structures, corresponding figures of merit (FOM's) for finding the correct solution are usually unsatisfactory (Cascarano, Giacovazzo & Viterbo, 1987). Two FOM's involving triplets (ALFCOMB and PSCOMB) are used in *SIR*, both based on the agreement between the theoretical and the experimental distributions of the α parameter for strong and PSI0 triplets respectively: the best agreement is characterized by unitary values of ALFCOMB

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Table 1. *For each crystal structure the space group, the main pseudotranslational vector* (**u**), *the average fractional scattering factor* (*sc*) *of the atoms suffering from pseudotranslational symmetry and various figures of merit are given*

	Space group	**u**	(sc×100)	ALFCOMB	PSCOMB	$(CFOM)_0$	CPHASE	CFOM
Freies	$P2_1/a$,	**a**/2+**b**/3	51	0·24	0·42	0·37	0·89	0·57
$AgPbSbS_3$	$Z=4$			(0·53)	(0·33)		(0·93)	
Meso	$Fdd2$,	**a**/3	68	0·56	0·82	0·70	0·64	0·67
$Ca_2Na_2Al_6Si_9O_{30}.8H_2O$	$Z=16$			(0·76)	(0·98)		(0·54)	
Ferri	$P2_1/n$,	(**a**+**b**)/2	55	0·96	0·88	0·92	1·00	0·96
$Fe_2(SO_4)_3$	$Z=4$			(0·98)	(0·91)		(1·00)	
Fega	$P6_3/mmc$,	**c**/3	44	0·72	0·43	0·59	1·00	0·76
$Fe_2Ga_2S_5$	$Z=2$			(0·98)	(0·77)		(1·00)	
Cime	Cc,	(**a**+**c**)/2	33	0·67	0·36	0·53	1·00	0·72
$C_{10}H_6N_6S.H_20$	$Z=4$			(0·92)	(0·87)		(1·00)	
Pocro	$B2/m$,	(**a**/6+**c**/2)	53	0·60	0·04	0·35	0·65	0·46
Cr_5KSe_8	$Z=2$			(0·17)	(0·11)		(0·99)	
Bobby	$P2_13$,	(**a**+**b**+**c**)/2	59	0·37	0·21	0·31	0·65	0·45
$CaNaN(CH_2CO_2)_3$	$Z=3$			(0·47)	(0·37)		(0·64)	

and PSCOMB. While for structures without remarkable superstructure effects such FOM's are actually near to unity (see Table 5 of Cascarano, Giacovazzo & Viterbo, 1987), occurrence of pseudotranslational symmetry usually prevents such an agreement because:

(*a*) pseudotranslational effects are sometime due to the simultaneous existence of more symmetry-independent pseudotranslational vectors, each operating on specific domains of the electron density. In the *SIR* probabilistic model the pseudotranslational symmetry always operates on the same domain;

(*b*) only the most important (up to three) pseudotranslational vectors are taken into account by *SIR*;

(*c*) both displacive and replacive deviations from ideality are usually present in real pseudotranslational symmetry. While the presence of the first type of deviation may be estimated by statistical calculations on diffraction intensities, the second type is not detectable at all. Thus the agreement between the mathematical model and the real structure cannot always be checked.

Some experimental results are shown in Table 1: for seven crystal structures [code names: Freies (Ito & Novacki, 1974); Meso (Adiwidjaja, 1972); Ferri (Christidis & Rentzeperis, 1975); Fega (Cascarano, Dogguy-Smiri & Nguyen-Huy Dung, 1987); Cime (Kojić-Prodić, Ružić-Toroš, Bresciani-Pahor & Randaccio, 1980); Pocro (Nguyen-Huy Dung, Vo-Van Tien, Behm & Beurskens, 1987); Bobby (Barnett, unpublished)] some useful crystallochemical parameters and the experimental values of ALFCOMB and PSCOMB are given, together with the value of the combined figure of merit (CFOM). The experimental values of ALFCOMB and PSCOMB are rather far from unity: in several cases their efficiency is not expected to increase remarkably if a more efficient phasing process could be used: indeed rather poor values of ALFCOMB and PSCOMB may be calculated from published phases (values in brackets).

In order to improve the situation we decided to explore how helpful the active use of one-phase structure seminvariants and how discriminating their passive use as a figure of merit, associated with the negative quartet figure of merit NQEST, may be.

One-phase structure seminvariants

If traditional $\sum_1$ relationships are used for estimating one-phase s.s.'s for structures with superstructure effects, often unrealistic reliability parameters are obtained. We have therefore modified $\sum_1$ relationships in order to take account of pseudotranslational symmetry: the seminvariant phase $\varphi_{\mathbf{H}}$ is estimated [see equation (IV.13)] by

$$\tan\varphi_{\mathbf{H}} \simeq \frac{\sum_{\mathbf{h},n} G(\mathbf{H},-\mathbf{h},\mathbf{h}\mathbf{R}_n)\sin 2\pi\mathbf{h}\mathbf{T}_n}{\sum_{\mathbf{h},n} G(\mathbf{H},-\mathbf{h},\mathbf{h}\mathbf{R}_n)\cos 2\pi\mathbf{h}\mathbf{T}_n} = \frac{A_{\mathbf{H}}}{B_{\mathbf{H}}}, \qquad (1)$$

with reliability parameter $G=(A_{\mathbf{H}}^2+B_{\mathbf{H}}^2)^{1/2}$. The **h** reflexions satisfy the condition $\mathbf{H}=\mathbf{h}(\mathbf{I}-\mathbf{R}_n)$,

$$G(\mathbf{H},-\mathbf{h},\mathbf{h}\mathbf{R}_n)=|E_{\mathbf{H}}|\varepsilon_{\mathbf{h}}[N(\mathbf{H},-\mathbf{h},\mathbf{h}\mathbf{R}_n)]^{-1/2}$$

and

$$[N(\mathbf{H},-\mathbf{h},\mathbf{h}\mathbf{R}_n)]^{-1/2}=\{1/S[\mathbf{h}_1,-\mathbf{h},\mathbf{h}\mathbf{R}_n]\}\times\{[(\beta/m)n_1^2n_2^2n_3^2\ldots][\textstyle\sum_3]_{\hat{p}}/\sum_N^{3/2}+[\sum_3]_q/\sum_N^{3/2}+g_1[\sum_3]_{p-\hat{p}}/\sum_N^{3/2}+g_2[\sum_3]_{p-\hat{p},\hat{p}}/\sum_N^{3/2}\},$$

$$\varepsilon_{\mathbf{h}}=R_{\mathbf{h}}^2-1.$$

It is noted that:

(i) one-phase s.s.'s which are substructure reflexions are estimated *via* 'sub-sub-sub' and 'sub-super-super' $\sum_1$ triplets, all of which are (in an average sense) reliable, no matter if deviations from ideal pseudotranslational symmetry occur. One-phase s.s.'s which are superstructure reflexions are estimated *via* 'super-sub-sub' and 'super-super-super' $\sum_1$ triplets, the second type of which is sometimes unreliable;

(ii) estimates involve $\varepsilon_{\mathbf{h}}$ values, so they critically depend on the efficiency of the renormalization process.

In spite of the above observations, estimates provided by (1) are rather reliable. As an example, in Table 2 the list of seminvariants is given for Pocro, together with their reliability parameters G: both superstructure and substructure ($h+3l=6n$) reflexions are in the list. Since the

Table 2. *Pocro: list of one-phase seminvariants with* $|E| \geq 1{\cdot}25$ *and their probabilistic estimates according to equation* (1)

φ_t is the true phase, an asterisk marks wrong indications.

h	k	l	E	G	φ_t	h	k	l	E	G	φ_t
0	0	4	1·75	86·7	0	14	6	0	1·86	1·0	π^*
0	0	2	1·41	66·7	0	8	−10	0	1·22	0·97	π
18	−2	0	1·62	21·3	0	0	6	4	1·97	0·96	0
0	12	0	1·39	14·8	0	2	−12	0	1·66	0·85	π
18	−2	2	2·31	14·5	0	2	−6	2	2·02	0·79	π
18	4	0	1·50	3·6	0	14	6	2	2·58	0·73	π^*
6	2	2	1·39	3·4	0	2	0	2	1·32	0·58	π
18	−8	0	1·54	2·5	0	12	0	4	1·73	0·53	π^*
18	4	2	2·14	2·4	0	14	−4	2	1·42	0·52	π
12	−6	4	1·66	2·2	0	6	−2	2	1·42	0·49	π^*
18	−8	2	2·26	1·5	0	16	−2	4	1·69	0·45	π
16	4	0	1·80	1·5	π	10	2	2	1·53	0·44	π
0	6	0	1·32	1·5	0	14	0	2	1·31	0·44	π^*
6	−4	2	1·24	1·5	0	4	2	4	1·54	0·43	π
6	4	2	1·43	1·5	0	14	2	2	1·37	0·39	π
4	2	0	1·25	1·4	π	22	2	2	1·36	0·39	π
16	−2	0	1·40	1·3	π	22	−6	2	1·43	0·38	π
2	−6	0	1·43	1·0	π	10	8	2	1·42	0·38	π
						22	0	2	1·66	0·31	π

first ones may be very useful for finding the correct solution among different trials, we decided to use all one-phase seminvariants in a passive way, as a sensitive FOM.

Negative quartet invariants

Quartets are estimated according to the formula given by Giacovazzo (1976), by using renormalized structure factors obtained by the procedure described in paper III. For the sake of simplicity no additional use of prior information on pseudotranslational symmetry is made. It is noted that:

(i) quartet invariants may be considered as a difference between triplets. If 'sub-sub-super' and 'super-super-super' triplets are algebraically impossible, only quartets can be formed such as

basis vectors	cross vectors
sub-sub-sub-sub	sub, sub, sub
sub-sub-super-super	sub, super, super
super-super-super-super	sub, sub, sub.

All of them are (in an average sense) reliable because they are based on interaction between 'sub-sub-sub' and 'sub-super-super' triplets.

(ii) If 'sub-sub-super' and 'super-super-super' are algebraically possible, 'sub-sub-sub-super' and 'super-super-super-sub' quartets can also be found, the reliability of which is at the moment unpredictable.

The CPHASE figure of merit suggested by Cascarano, Giacovazzo & Viterbo (1987) has been calculated (as a combination of one-phase seminvariants and NQEST figures of merit) for the seven structures quoted in Table 1. Even if no prior information on pseudotranslational symmetry was used for estimating quartet invariants, CPHASE unexpectedly proved to be the most efficient FOM (the maximum value of CPHASE always picks up the solution) and the least sensitive to disturbing superstructure effects (its values are usually close enough to unity). As a consequence, for structures with superstructure effects, *SIR* default weights associated with the various FOM's for calculating the combined figure of merit CFOM have been modified, from

$$W(\text{ALFCOMB}) = 1{\cdot}0 \qquad W(\text{PSCOMB}) = 1{\cdot}4$$
$$W(\text{CPHASE}) = 1{\cdot}0$$

to

$$W(\text{ALFCOMB}) = 1{\cdot}0 \qquad W(\text{PSCOMB}) = 1{\cdot}0$$
$$W(\text{CPHASE}) = 1{\cdot}4.$$

The new most satisfactory values of CFOM are shown in the last column of Table 1.

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