

- MAMEDOV, KH. S. & BELOV, N. V. (1956). *Dokl. Akad. Nauk SSSR*, **107**, 463–466.
- MORALES, J., JEFFERSON, D. A., HUTCHINSON, J. L. & THOMAS, J. M. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1834–1836.
- MARESCH, W. V. & MOTTANA, A. (1976). *Contrib. Mineral. Petrol.* **55**, 69–79.
- OHASHI, Y. & FINGER, L. W. (1975). *Ann. Rep. Carnegie Inst. Washington*, **74**, 564–569.
- PEACOR, D. R. & BUERGER, M. J. (1962). *Z. Kristallogr.* **117**, 331–343.
- PREWITT, C. T. (1967). *Z. Kristallogr.* **125**, 298–316.
- ROGERS, G. L. (1969). *J. Microsc. (Oxford)*, **89**, 121–124.
- THOMAS, J. M. & JEFFERSON, D. A. (1978). *Endeavour*, **2**, 127–136.
- WADSLEY, A. D. (1964). *Non-Stoichiometric Compounds*, Ch. 3, edited by L. MANDELKOM. London: Academic Press.

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Effects of Phase Errors on *E* Maps

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Abstract

A systematic investigation of the effect of phase errors of different types on *E* maps is presented. Both random and systematic errors have been considered with distributions depending in different ways on the resolution of the data. Considerably large random errors can be tolerated without great loss of structural information in the *E* maps, while smaller systematic errors have greater destructive effects. These effects are explained by the introduction and analysis of a phase-error function.

Introduction

The final outcome of any direct-methods procedure is a set of approximate phases with which an *E* map is computed. It is obvious that the quality of the map is related to the errors in the phases and it is this relationship which we study in this work. The interest of this analysis is also related to the possibility of comparing the power of different direct-methods procedures, from tests on known structures, by giving the value of the mean phase error or the root-mean-square deviation of the phases.

Phase errors and resolution

Parthasarathy (1978), assuming a normal distribution for the errors of the atomic positions, has calculated the

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average of the absolute value of the phase errors, $\langle |\Delta\phi| \rangle$, as a function of the average of the absolute value of the coordinate errors, $\langle |\Delta r| \rangle$, for different resolutions. An analysis of Fig. 1‡ shows that, at a given value of $\langle |\Delta r| \rangle$, the phase error is high at high resolution and low at low resolution. For instance, we can see that for $\langle |\Delta r| \rangle = 0.4 \text{ \AA}$ the corresponding phase error is 70° at a resolution of 0.77 \AA , while it is 13° at $R = 5 \text{ \AA}$.

From Fig. 1 we have graphically derived Fig. 2 which within the error of the graphical derivation shows a linear trend of $\langle |\Delta r| \rangle$ as a function of the resolution for different values of $\langle |\Delta\phi| \rangle$. The extrapolation of these lines to $R = 0$ indicates that, when assuming a normal distribution for Δr , with an infinite set of data the structure is exactly defined even when the average phase error is very close to 90° ($\langle |\Delta\phi| \rangle = 90^\circ$ corresponds to completely random phases).

From these observations we can infer that it is more important to consider not only the overall average phase error but also the distribution of the error as a function of the resolution. In fact, as far as the consequences on the accuracy of the atomic positions is concerned, a set of phases with relatively high overall $\langle |\Delta\phi| \rangle$, due to large errors in the high-angle reflexions, will be preferable to the same set of reflexions with smaller $\langle |\Delta\phi| \rangle$ but with large errors in the low-angle reflexions.

In order to verify this hypothesis we have performed some tests on the known structure of a photolysis product (Karle, Karle & Estlin, 1967) (KARLE: $P2_1 2_1 2_1$, 17 atoms in the asymmetric unit). Using a routine which generates random numbers with a normal

‡ Fig. 1 is a reproduction of Fig. 3(a) of the paper by Parthasarathy (1978) with a modified notation.

distribution, with a given σ and average equal to zero, we have generated phase errors to apply to the correct phases.* The reflexions were divided into n equally populated shells of reciprocal space with increasing resolution and the errors were generated in three different ways:

(i) the σ was increased from one shell to the other and the linear increase was defined by giving the values for $\sigma(1)$ and $\sigma(n/2)$;

(ii) the σ was constant for all shells;

(iii) the σ was decreased and the linear decrement was defined by giving the values for $\sigma(n/2)$ and $\sigma(n)$.

For the special reflexions the phase error was set to 0° when the computed error was less than 90° and set to 180° when the error was greater than 90° .

In Fig. 3 the distributions of the actual r.m.s.d.'s of the phases as a function of the shell number (*i.e.* the resolution) are shown for the following phase-error distributions:

(i) $\sigma(1) = 10^\circ$, $\sigma(n/2) = 75^\circ$ (curve $\triangle - \triangle - \triangle$, incr.);

(ii) $\sigma(\text{constant}) = 75^\circ$ (curve $\bullet - \bullet - \bullet$, const.);

(iii) $\sigma(n) = 10^\circ$, $\sigma(n/2) = 75^\circ$ (curve $\circ - \circ - \circ$, decr.).

* In fact a normal distribution is not the correct distribution to deal with cyclic variables (see Giacovazzo, 1979); nevertheless it is a very simple way for introducing phase errors with σ well approximating the desired values. On the other hand, we use that distribution simply as a way to generate errors but we do not attempt to analyse the properties of the f maps for different kinds of error distributions. We thank one of the referees for pointing out this matter.

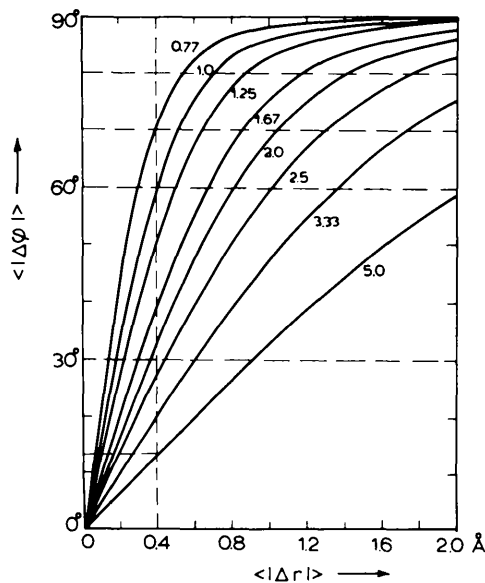


Fig. 1. Average phase error, $\langle |\Delta\phi| \rangle$, as a function of the positional error $\langle |\Delta r| \rangle$ for different fixed values of the resolution R . (Derived from Parthasarathy, 1978, Fig. 3a.)

In each case an E map was calculated with the *FFT* program of *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The map was interpreted by the *SEARCH* routine and finally the positions of the peaks were compared with the known coordinates. The results of this procedure are summarized in Table 1 for the three cases illustrated in Fig. 3 and for four other tests. In the first column we indicate the type of distribution with, in parentheses, the values of σ . The second and third columns show the actual overall r.s.m.d. and mean phase error. The last part of the table shows the percentage of peaks with deviation from the correct atomic position $|\Delta r| < 0.1, 0.2, 0.3, 0.5, 0.75, 1.0 \text{ \AA}$.

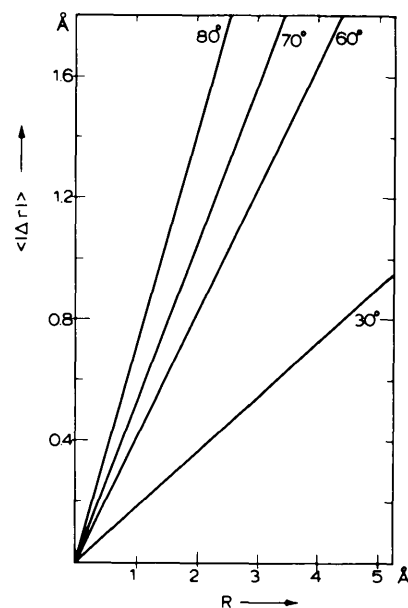


Fig. 2. Average positional error $\langle |\Delta r| \rangle$ as a function of the resolution R for different fixed values of the average phase error $\langle |\Delta\phi| \rangle$. (Derived from Fig. 1).

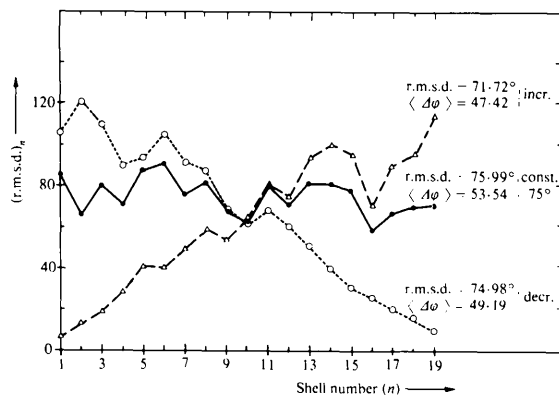


Fig. 3. KARLE. Examples of different random phase-error distributions as a function of the resolution (expressed as the sequential number of the shell into which the reciprocal lattice has been subdivided).

Table 1. *KARLE*: analysis of the *E* maps produced with different types of random phase-error distributions

Distribution	r.m.s.d.	$\langle \Delta\phi \rangle$	% of atoms with $ \Delta r <$					
			0.1	0.2	0.3	0.5	0.75	1.0 Å
Const. (75°)	75.99°	53.54°	18	64	88	88	94	94
Incr. (10°, 75°)	71.72	47.42	29	88	94	100	100	100
Decr. (10°, 75°)	74.98	49.19	35*	82	88	94	94	94
Const. (95°)	92.03	68.78	6	17	41	53	59	59
Incr. (20°, 95°)	86.83	62.54	12	41	52	88	88	88
Decr. (20°, 95°)	90.07	65.03	6	29	59	59	59	59
Incr. (30°, 75°)	72.49	49.49	29	76	100	100	100	100
Decr. (30°, 75°)	76.35	52.05	24	70	76	82	82	82

In general the results show that for a set of phases with similar r.m.s.d., more atomic positions can be found within the various limits of $|\Delta r|$ in the case of an increasing distribution than in the case of constant and decreasing distributions. On the other hand the particular result marked * in Table 1 is not really surprising. In a first approximation we can say that the low-resolution reflexions define the skeleton of the structure and the high-resolution reflexions define the details to be superposed on it. The case of decreasing errors with resolution corresponds to superposing very accurate details on a wrong skeleton. Then, if by chance details are superposed on highly positive regions, some atoms will be found with very accurate coordinates. We can conclude by saying that in the case of decreasing errors only part of the structure and some atoms with very accurate coordinates are likely to be found. Conversely, in the case of increasing errors it is more likely for a larger part of the structure to be found but with less accurate coordinates. But the most striking fact emerging from Table 1 is that even with large r.m.s.d.'s it is possible to identify most of the structure.

The phase-error function

In order to see whether the unexpected results of these tests are due to the randomness of the generated errors and to have a better understanding of the effects of phase errors on *E* maps, we introduce what we call *the phase-error function*. A structure factor with phase error is related to the correct structure factor by

$$E(\text{err}) = E(\text{corr}) \exp(2\pi i \Delta\phi), \quad (1)$$

where $\Delta\phi$ is the phase error. By applying the convolution theorem this relation becomes, in direct space,

$$\rho(\text{err}) = \rho(\text{corr}) * f, \quad (2)$$

where *f* is the phase-error function, that is

$$f(\mathbf{r}) = \sum_{\mathbf{h}} \exp(2\pi i \Delta\phi_{\mathbf{h}}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}). \quad (3)$$

From (2) we can see that if *f* has just a peak at the origin and a relatively small background level, then

$\rho(\text{err}) \simeq \rho(\text{corr})$. On the other hand, if in the *f* map there are one or more peaks relatively high with respect to the origin peak, then its convolution with $\rho(\text{corr})$ will produce a superposition of displaced structures and the resulting map will not be interpretable. The phase-error function provides a means for characterizing a kind of phase error that will lead to uninterpretable maps: they must produce one or more large non-origin peaks in the *f* map. It is evident from (3) that this happens when the phase errors for a subset of reflexions are of the form $\Delta\phi = -\mathbf{h} \cdot \mathbf{t}$. In this case the peak in the *f* map will be at **t**.

The above considerations can explain why direct-methods procedures produce at times sets of phases leading to the correct structure (or a fragment of it) with correct orientation but in a wrong position. The error in the phases in this case are systematic in the sense explained and they produce in the *f* map a peak at **t**, which corresponds to a displacement from the correct position.

It is also clear why, with phases affected by normally distributed errors, we can see most of the structure even with large values of $\langle |\Delta\phi| \rangle$; *i.e.* such phase errors will not, in general, produce large non-origin peaks. As shown by the examples reported in the next paragraph, the effect of increasing the overall $\langle |\Delta\phi| \rangle$ is just to reduce the height of the origin peak in relation to the background. Because the data are finite, when $\langle |\Delta\phi| \rangle$ becomes very large some secondary peaks appear in the *f* map even with errors normally distributed. In the ideal case of an infinite set of data we would expect to have just a peak at the origin for any value of $\langle |\Delta\phi| \rangle < 90^\circ$ and this would explain the behaviour of the lines in Fig. 2 when extrapolated to $R = 0$. Some other theoretical studies of the properties of the phase-error function are in progress.

Examples

In order to verify these ideas we have performed some further tests on two known structures: 3-chloro-1,3,4-triphenyl-2-azetidinone (Colens, Declerq, Germain,

Table 3. ERGO: analysis of the *E* maps and of the *f* maps obtained with different types of random phase-error distributions

Distribution	r.m.s.d. $\langle \Delta\phi \rangle$	<i>E</i> map						<i>f</i> map								Background level	
		% atoms with $ \Delta\phi <$						Peak numbers (height & distance from 0)									
		0.1	0.2	0.3	0.5	0.75	1.0 Å	1	2	3	4	5	10	20	40	60	
Const. (45)	43.06 27.80	67	95	100	100	100	100	1378 0.12	333 1.44	303 1.51	259 1.48	228	168	112	93	87	{ -85 90
Const. (60)	62.15 41.74	50	86	98	100	100	100	1087 0.13	241 1.48	239 1.49	222 1.52	194	145	121	111	102	{ -100 100
Const. (80)	79.80 56.64	27	65	79	88	88	88	690 0.13	212 1.37	201 1.60	201 1.35	189	144	134	121	114	{ -115 110
Incr. (20, 90)	85.70 60.82	5	27	57	86	91	96	608 0.18	167 1.48	158 2.44	156 3.75	144	133	124	117	110	{ -115 115
Decr. (20, 90)	88.23 63.03	17	53	66	69	69	69	585 0.08	386 1.35	358 1.36	198 1.49	178	154	131	119	114	{ -110 100

Table 4. ERGO: Analysis of the *E* maps and of the *f* maps obtained using three sets of phases generated by MULTAN

MULTAN set	r.m.s.d. $\langle \Delta\phi \rangle$	<i>E</i> map						<i>f</i> map								Background level	
		% atoms with $ \Delta\phi <$						Peak numbers (height & distance from 0)									
		0.1	0.2	0.3	0.5	0.75	1.0 Å	1	2	3	4	5	10	20	40	60	
Set 1	53.90° 30.55	14	55	66	75	81	82	1363 0.12	559 1.40	530 4.48	518	484	441	410	377	357	{ -250 250
Set 7	56.47 33.71	8	50	72	75	80	81	1311 0.12	572 8.18	540 11.9	507	482	434	412	386	360	{ -250 250
Set 4	83.03 56.98	0	9	29	38	46	56	626 0.12	539 1.60	524 5.25	508	505	475	420	394	369	{ -250 250

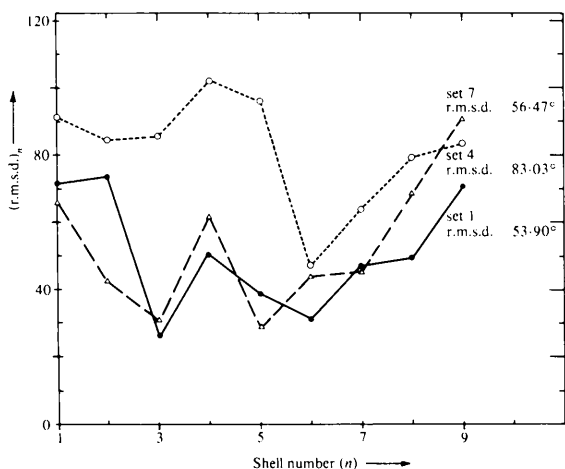


Fig. 4. ERGO. Phase-error distributions of three sets of phases generated by MULTAN.

Conclusions

The analysis that we have carried out has revealed some features of the relationship between phase errors and structural information in an *E* map. In particular, the effect of systematic errors in making the *E* maps less interpretable seems of great importance. Thus, it is less serious to have relatively large random errors than to have smaller but systematic errors. Also, the effect of the phase-error distribution as a function of the resolution indicates that we should be very careful in accurately phasing the low-resolution reflexions.

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References

- COLENS, A., DECLERQ, J. P., GERMAIN, G., PUTZEYS, J. P. & VAN MEERSSCHE, M. (1974). *Cryst. Struct. Commun.* **3**, 119–122.
- GIACOVAZZO, C. (1979). *Acta Cryst.* **A35**, 757–764.
- HULL, S. E., LEBAN, I., MAIN, P., WHITE, P. S. & WOOLFSON, M. M. (1976). *Acta Cryst.* **B32**, 2374–2381.
- KARLE, I. L., KARLE, J. & ESTLIN, J. A. (1967). *Acta Cryst.* **23**, 494–500.
- MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England and Louvain, Belgium.
- PARTHASARATHY, S. (1978). *Acta Cryst.* **A34**, 512–516.
- WRIGHT, H. & WOOLFSON, M. M. (1979). Private communication.

SHORT COMMUNICATIONS

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The defect structure of VO_x: comparison between X-ray and electron diffraction. By M. MORINAGA, *Toyohashi University of Technology, Toyohashi, Aichi 440, Japan* and J. B. COHEN, *Department of Materials Science and Engineering, The Technological Institute, Northwestern University, Evanston, Illinois 60201, USA*

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Abstract

Discrepancies exist in the local atomic arrangements determined from diffuse X-ray and electron scattering. The possible reasons for this are examined.

In VO_x (0.8 < *x* < 1.3) there are large numbers of both anion and cation vacancies and interstitial cations. The concentrations of these vary with composition, *x*. The presence of (composition-dependent) diffuse scattering indicates that these defects are not randomly arranged. The purpose of this communication is to compare our results on the defect arrangement in VO_x (Morinaga & Cohen, 1979*a,b*) from studies of diffuse X-ray scattering with those deduced by Andersson and co-workers from their pioneering attempt to analyze quantitatively diffuse electron scattering (Andersson, Gjönnes & Taftö, 1974; Andersson, Gjönnes & Forouh, 1978; Anderson, 1979).

This comparison is presented in Table 1. While there are similarities there are also serious differences. Besides complex dynamical effects in electron diffraction, the problem in estimating background scattering makes it difficult to obtain quantitative information on local order, because a weak modulation of diffuse intensity in reciprocal space cannot be measured accurately. An advantage of the X-ray method is that this kind of problem can be treated with measurements of diffuse intensities in absolute units so that all sources of

the scattering can in principle be found. Other origins for the discrepancies that appear in Table 1 may be due to the regression method used for the analysis of diffuse electron scattering. This method is quite sensitive to the choice of fitting parameters and fitting regions in reciprocal space (Morinaga, 1978). Least-squares fitting using a limited number of parameters and restricted regions of reciprocal space sometimes yields erroneous or unstable results. Andersson and co-workers (Andersson *et al.*, 1978; Andersson, 1979) analyzed data on a few reciprocal planes with a small number of parameters. In addition, an electron microscope with an accelerating voltage of 1 MeV was employed. A wide range of reciprocal space can be measured with such an instrument, and the diffuse scattering at the highest scattering angles was used by Andersson *et al.* to detect the static and dynamic displacements of ions. But the contribution of higher-order displacements to the measured intensity is appreciable in this region. This results in problems in estimating the first- and second-order displacement coefficients in the presence of these (ignored) higher-order terms. Thus, there are several difficulties to be resolved in quantitative studies of diffuse electron scattering. On the other hand, the X-ray method averages over a much larger volume of sample than the electron method; anisotropic local structures can be lost in this averaging. Furthermore, there could be local differences in composition, and hence in the atomic arrangements, which are best examined with electron scattering. Furthermore, the X-ray method is not nearly as rapid as the electron method. But at this time it is more