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A Simple Rule for Finding and Distinguishing Triplet Phase Invariants with Values Near 0 or π with Isomorphous Replacement Data

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Abstract

On the basis of some mathematical and physical characteristics of isomorphous-replacement experiments, it has been possible to derive a simple rule called R_{iso} that permits the selection of those triplet phase invariants that have values close to zero or π . Test examples show that large numbers of invariants may be evaluated by means of R_{iso} with reliabilities that are potentially high, but depend, of course, on the reliability of the experimental data. In order to apply the rule, it is not necessary to know the chemical nature of the substituent atoms, their positions in the structure or their occupancy. The rule R_{iso} affords new insights into the inter-relationships among isomorphous-replacement data and an alternative selection method to the use of the conditional joint probability distribution. A formula has also been derived for estimating the value of the cosine of triplet phase invariants for the native substance, $\cos(\varphi_{hP} + \varphi_{kP} + \varphi_{(h+k)P})$, in terms of measured structure-factor magnitudes and structure-factor magnitudes associated with the contribution from substituent atoms.

Introduction

Isomorphous-replacement experiments provide information that is quite useful in selection procedures for finding large numbers of triplet phase invariants, whose values are close to zero or π , even in very complex structures. One such procedure has already been described by Hauptman (1982a), in which the concept of the conditional joint probability distribution has been applied to the isomorphous-replacement technique, resulting in a formula whose validity has been demonstrated in an extensive test calculation (Hauptman, Potter & Weeks, 1982). The various conceptual aspects and features of the joint probability distribution distinguish the latter approach from the one pursued in this article.

The joint probability distribution, as generally used in crystallography and from which the conditional distribution is derived, may be viewed as counting the relative number of atomic configurations (each given unit weight) associated with some infinitesimal volume in the space of the variables, say $E_1, \dots, \varphi_1, \dots$. In those cases where some small region of the space is

associated with a disproportionately large fraction of the possible atomic configurations, the values of the variables can be determined within narrow bounds. Such a circumstance can be interpreted as indicating that the values of the variables are known within narrow ranges with high probability, since most, by far, of the possible atomic configurations are consistent with those values of the variables, and the unknown configuration or structure of interest is likely to be among them. A conditional distribution derivable from the joint probability distribution answers the question 'What relative density of only those atomic configurations that are compatible with given fixed values of some of the initial variables is to be associated with particular values of the remaining variables?'

This is illustrated in Fig. 1 in which the quantity Ω could represent the possible values of a triplet phase invariant. The ordinate can simply be labeled $P(\Omega)$ or, alternatively, it can represent the relative density of all those configurations that give specific fixed values for six structure-factor magnitudes assumed to be known for a triplet phase invariant in an isomorphous-replacement experiment. The sharply peaked distribution shows that most of the configurations, among which the configuration of the crystal structure of interest is likely to be found, favor values for the triplet invariant within narrow bounds. We can then pick the value of the maximum of the distribution, and expect it to represent the triplet invariant with high probability and small variance. The flatter distribution in Fig. 1 would not be useful. There would be little assurance that the broad maximum would be related to the structure of interest. If use of the relative number of atomic configurations associated with particular values of the variables is inherent in the derivation of the joint probability distribution, it is necessary to know the chemical composition of the structure of interest.

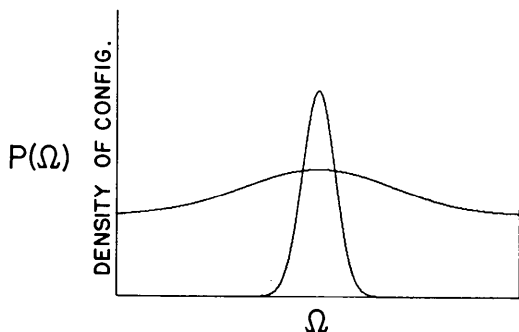


Fig. 1. A fairly sharply peaked and a relatively flat probability distribution. The main point of this figure is to emphasize that the probability density $P(\Omega)$ is based on the density of atomic configurations, *i.e.* those values of Ω associated with the greatest densities of atomic configurations are considered the most probable.

In this article, the analysis is based on some simple physical and mathematical properties associated with isomorphous-replacement experiments. These concern observations related to the differences of the magnitudes of the structure factors for the substituted and unsubstituted structures and the expected values of triplet phase invariants associated with the 'heavy'-atom structure. This approach does not require the scanning of atomic configurations nor is there a need to know the chemistry of the structure of interest or of the substituent atoms. The result is a simple rule, based on the observed structure-factor magnitudes, that permits the selection of triplet phase invariants whose values are close to zero or π .

Conceptual basis

The concepts involved in the development of the rule of interest are illustrated in Fig. 2. In this diagram, the larger circle has a diameter $|F_{PH}|$, a structure-factor magnitude associated with the combination of the unsubstituted structure (P) and substituent atoms (H). The smaller circle has a diameter $|F_p|$, a structure-factor magnitude associated with the unsubstituted structure. The quantity F_H is the structure factor for the substituent atoms.

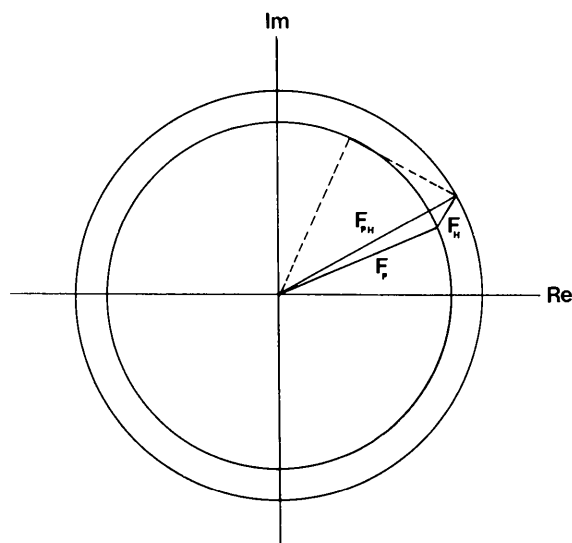


Fig. 2. An illustration of the vector equation, $F_{PH} = F_p + F_H$. The largest magnitude differences, $||F_{PH}| - |F_p||$, are associated with the largest possible values of $|F_H|$. This case is represented by the triangle formed from solid lines. The placement of the dotted line, representing an alternative position for F_p , would not be possible if the magnitude of the dotted line connecting it to F_{PH} would exceed the maximum possible value. This implies that, for the largest magnitude differences, the phase angles for F_{PH} and F_p do not differ by much.

The solid lines forming a closed triangle in Fig. 2 represent the vector equation

$$\mathbf{F}_H = \mathbf{F}_{PH} - \mathbf{F}_P. \quad (1)$$

Given, for example, the vector \mathbf{F}_{PH} as in Fig. 2, the dotted line of radius $|\mathbf{F}_P|$ could perhaps be a possible location for \mathbf{F}_P , but not necessarily. It would not be possible if the dotted line connecting this vector with \mathbf{F}_{PH} would have to have a magnitude that exceeds the maximum possible value for $|\mathbf{F}_H|$. The implication of this observation is that if the largest differences $|\mathbf{F}_{PH}| - |\mathbf{F}_P|$ are selected from a data set, they would be associated with the largest possible values of $|\mathbf{F}_H|$ and \mathbf{F}_{PH} and \mathbf{F}_P would have phases that do not differ greatly. We formalize these observations and their implications as follows:

1. The largest magnitude differences, $|\mathbf{F}_{PH}| - |\mathbf{F}_P|$, are associated with the largest values of the magnitudes $|\mathbf{F}_H|$.

2. Triplet phase invariants associated with the largest $|\mathbf{F}_{hH}\mathbf{F}_{kH}\mathbf{F}_{(\tilde{h}+\tilde{k})H}|$ can be expected to have values close to zero, especially for simple heavy-atom structures.

3. For the larger values of $|\mathbf{F}_{PH}| - |\mathbf{F}_P|$, the phase of \mathbf{F}_P , ϕ_P , will differ little in value from the phase of \mathbf{F}_{PH} , ϕ_{PH} .

Theory

Derivation of R_{iso}

We start with (1), add additional subscripts to indicate the association of structure factors with reciprocal vectors and form the products

$$\begin{aligned} \mathbf{F}_{hH}\mathbf{F}_{kH}\mathbf{F}_{(\tilde{h}+\tilde{k})H} &= (\mathbf{F}_{hPH} - \mathbf{F}_{hP})(\mathbf{F}_{kPH} - \mathbf{F}_{kP}) \\ &\times (\mathbf{F}_{(\tilde{h}+\tilde{k})PH} - \mathbf{F}_{(\tilde{h}+\tilde{k})P}). \end{aligned} \quad (2)$$

$$\begin{aligned} |\mathbf{F}_{hH}\mathbf{F}_{kH}\mathbf{F}_{(\tilde{h}+\tilde{k})H}| \exp[i(\phi_{hH} + \phi_{kH} + \phi_{(\tilde{h}+\tilde{k})H})] \\ = |\mathbf{F}_{hPH}\mathbf{F}_{kPH}\mathbf{F}_{(\tilde{h}+\tilde{k})PH}| \exp[i(\phi_{hPH} + \phi_{kPH} + \phi_{(\tilde{h}+\tilde{k})PH})] \\ - |\mathbf{F}_{hPH}\mathbf{F}_{kP}\mathbf{F}_{(\tilde{h}+\tilde{k})PH}| \exp[i(\phi_{hPH} + \phi_{kP} + \phi_{(\tilde{h}+\tilde{k})PH})] \\ - |\mathbf{F}_{hPH}\mathbf{F}_{kPH}\mathbf{F}_{(\tilde{h}+\tilde{k})P}| \exp[i(\phi_{hPH} + \phi_{kPH} + \phi_{(\tilde{h}+\tilde{k})P})] \\ + |\mathbf{F}_{hPH}\mathbf{F}_{kP}\mathbf{F}_{(\tilde{h}+\tilde{k})P}| \exp[i(\phi_{hPH} + \phi_{kP} + \phi_{(\tilde{h}+\tilde{k})P})] \\ - |\mathbf{F}_{hP}\mathbf{F}_{kPH}\mathbf{F}_{(\tilde{h}+\tilde{k})PH}| \exp[i(\phi_{hP} + \phi_{kPH} + \phi_{(\tilde{h}+\tilde{k})PH})] \\ + |\mathbf{F}_{hP}\mathbf{F}_{kP}\mathbf{F}_{(\tilde{h}+\tilde{k})PH}| \exp[i(\phi_{hP} + \phi_{kP} + \phi_{(\tilde{h}+\tilde{k})PH})] \\ + |\mathbf{F}_{hP}\mathbf{F}_{kPH}\mathbf{F}_{(\tilde{h}+\tilde{k})P}| \exp[i(\phi_{hP} + \phi_{kPH} + \phi_{(\tilde{h}+\tilde{k})P})] \\ - |\mathbf{F}_{hP}\mathbf{F}_{kP}\mathbf{F}_{(\tilde{h}+\tilde{k})P}| \exp[i(\phi_{hP} + \phi_{kP} + \phi_{(\tilde{h}+\tilde{k})P})]. \end{aligned} \quad (3)$$

On the basis of observation 3 above, (3) may be written, to good approximation,

$$\begin{aligned} |\mathbf{F}_{hH}\mathbf{F}_{kH}\mathbf{F}_{(\tilde{h}+\tilde{k})H}| \exp[i(\phi_{hH} + \phi_{kH} + \phi_{(\tilde{h}+\tilde{k})H})] \\ \simeq (|\mathbf{F}_{hPH}| - |\mathbf{F}_{hP}|)(|\mathbf{F}_{kPH}| - |\mathbf{F}_{kP}|)(|\mathbf{F}_{(\tilde{h}+\tilde{k})PH}| \\ - |\mathbf{F}_{(\tilde{h}+\tilde{k})P}|) \exp[i\langle\phi_h + \phi_k + \phi_{\tilde{h}+\tilde{k}}\rangle], \end{aligned} \quad (4)$$

where $\langle\phi_h + \phi_k + \phi_{\tilde{h}+\tilde{k}}\rangle$ represents the average of the eight triplet phase invariants on the right side of (3).

On the basis of observations 1 and 2 above, the left side of (4) is essentially a real positive number and if the heavy atoms have a centric configuration in the unit cell, it is precisely so. Therefore, when the triple product on the right side of (4) is composed of large magnitude differences, an examination of this equation leads to the following rule:

Rule, R_{iso} : If the sign of the product of the magnitude differences, $(|\mathbf{F}_{hPH}| - |\mathbf{F}_{hP}|)(|\mathbf{F}_{kPH}| - |\mathbf{F}_{kP}|)(|\mathbf{F}_{(\tilde{h}+\tilde{k})PH}| - |\mathbf{F}_{(\tilde{h}+\tilde{k})P}|)$, is plus, the value of the average invariant, $\langle\phi_h + \phi_k + \phi_{\tilde{h}+\tilde{k}}\rangle$, is close to zero and if the sign of the product is minus, the value of the average invariant is close to π .

This rule, in effect, assigns the estimate to all eight triplet invariants in (3). As a modification of R_{iso} , the estimates may be assigned only to those triplet phase invariants that are associated with the larger products of structure-factor magnitudes listed among the eight possibilities given in (3), instead of to all eight of them. Test calculations indicate that improved accuracy may be obtained this way.

The effect of rescaling the F , to represent approximately structure factors from point atoms, on the application of R_{iso} has not yet been investigated. The question is whether optimal application of R_{iso} would involve use of F for real atoms or point atoms or both types or even some intermediate form.

Interpretation of the triple product of magnitude differences

We now investigate the meaning of

$$\begin{aligned} (|\mathbf{F}_{hPH}| - |\mathbf{F}_{hP}|)(|\mathbf{F}_{kPH}| - |\mathbf{F}_{kP}|) \\ \times (|\mathbf{F}_{(\tilde{h}+\tilde{k})PH}| - |\mathbf{F}_{(\tilde{h}+\tilde{k})P}|) \end{aligned} \quad (5)$$

under the circumstances that the differences are of large magnitude and the contribution, \mathbf{F}_H , of the substituted atoms is much smaller in magnitude than the contribution from the remaining atoms, \mathbf{F}_P . This usually pertains with macromolecules.

It follows from (1) that

$$\begin{aligned} |\mathbf{F}_{hPH}|^2 &= |\mathbf{F}_{hP}|^2 + |\mathbf{F}_{hH}|^2 + 2|\mathbf{F}_{hP}||\mathbf{F}_{hH}| \\ &\times \cos(\phi_{hP} - \phi_{hH}). \end{aligned} \quad (6)$$

Since it is assumed that $|\mathbf{F}_{hH}| \ll |\mathbf{F}_{hP}|$, we have, to good approximation,

$$|\mathbf{F}_{hPH}| - |\mathbf{F}_{hP}| \simeq |\mathbf{F}_{hH}| \cos(\phi_{hP} - \phi_{hH}). \quad (7)$$

If the product (5) is formed from (7), we obtain the factor

$$\begin{aligned} \cos(\phi_{hP} - \phi_{hH}) \cos(\phi_{kP} - \phi_{kH}) \\ \times \cos(\phi_{(\tilde{h}+\tilde{k})P} - \phi_{(\tilde{h}+\tilde{k})H}) = C_3. \end{aligned} \quad (8)$$

By use of the addition theorem for cosines, it can be easily shown that

$$C_3 = \frac{1}{4}[\cos J + \cos(J - 2\varphi_{hP} + 2\varphi_{hH}) + \cos(J - 2\varphi_{kP} + 2\varphi_{kH}) + \cos(J - 2\varphi_{(\bar{h}+\bar{k})P} + 2\varphi_{(\bar{h}+\bar{k})H})], \quad (9)$$

where

$$J = \varphi_{hP} + \varphi_{kP} + \varphi_{(\bar{h}+\bar{k})P} - \varphi_{hH} - \varphi_{kH} - \varphi_{(\bar{h}+\bar{k})H}. \quad (10)$$

It is seen that J is composed of a triplet phase invariant for the structure P and a corresponding one for the substituent atoms.

Examination of (7) shows that the largest differences in magnitude occur when $\cos(\varphi_{hP} - \varphi_{hH})$ is close to +1 or -1, i.e. the two angles differ approximately by zero(mod 2π) or by π (mod 2π). Therefore, the difference, $2\varphi_{hP} - 2\varphi_{hH}$, is approximately zero(mod 2π). This observation permits us to approximate (9) to

$$C_3 \simeq \cos J \quad (11)$$

and so, by use of (8) and (11), the triple product of differences formed from (7), and the high probability that the triplet phase invariant for the H structure has a value close to zero, we obtain the formula for a triplet phase invariant associated with the P structure,

$$\begin{aligned} \cos(\varphi_{hP} + \varphi_{kP} + \varphi_{(\bar{h}+\bar{k})P}) \simeq & \{ (|F_{hPH}| - |F_{hP}|) \\ & \times (|F_{kPH}| - |F_{kP}|) \\ & \times (|F_{(\bar{h}+\bar{k})PH}| - |F_{(\bar{h}+\bar{k})P}|) \} \\ & \times [|F_{hH}F_{kH}F_{(\bar{h}+\bar{k})H}|]^{-1}. \end{aligned} \quad (12)$$

Expression (12) shows once again that the sign of the triple product of the magnitude differences determines whether the phase invariant is close to zero or close to π .

It would appear from (12) that given information concerning the denominator on the right side, it might

be possible to make an approximate determination of the value of the cosine of the invariant. The usefulness of (12) in this respect is very much dependent upon the accuracy of the experimental data.

Test calculations

Model calculations were performed on quinidine sulfate, $(C_{20}H_{25}N_2O_2)_2SO_4 \cdot 2H_2O$ (Karle & Karle, 1981), which crystallizes in space group $P2_1$. In order to form isomorphous pairs, with relative scattering power between the H and P structures comparable to that in macromolecules, two artificial pairs were created by defining, in one case, the native substance (P) as the structure with sulfur removed and the heavy-atom derivative (PH) as the complete molecule, and, in the second case, the native substance as the structure with sulfur and one oxygen atom removed and the heavy-atom derivative as the structure obtained by replacing the missing sulfur and oxygen atoms by two magnesium atoms. Both isomorphous pairs gave the same general results. Products of magnitude differences, as appear on the right side of (4), were generally composed from the 150 largest magnitude differences and ordered with the largest product first. Hundreds of triplet phase invariants were estimated to be 0 or π by use of *Rule*, R_{iso} , as indicated in Tables 1 and 2. The factor ($\times 8$) in Tables 1 and 2 implies that all eight triplet phase invariants on the right side of (3) are evaluated by the estimates. This is also indicated by the letter A which implies that the average values of the sets of eight invariants are used to estimate the average errors. In the case of centric reflections for which the triplet phase invariants must have the value of 0 or π , all the estimates made were correct without exception and all eight triplet phase invariants, as listed on the right side of (3), were found to have the same value. For the invariants composed from acentric reflections, Tables 1 and 2 show that an improvement in accuracy

Table 1. Estimates of values of triplet phase invariants from isomorphous replacement for quinidine sulfate based on isomorphous pair formed from presence and absence of sulfur

Type of invariant	Number of data	Number of invariants	Estimate	Actual average value	Invariant selection*	Average error (rad)
Centric	516	62($\times 8$)	0	0	A	0
Centric	516	38($\times 8$)	π	π	A	0
Acentric	2354	54	0	0.13	L	0.38
Acentric	2354	45	π	-2.93	L	
Acentric	2354	55($\times 8$)	0	0.04	A	0.57
Acentric	2354	45($\times 8$)	π	-2.99	A	
Acentric	2354†	100	0	-0.05	L	0.30

* L means errors and averages are based on the value of the triplet phase invariant associated with the largest product of structure-factor magnitudes and A means that they are based on the average values of the eight possible invariants formed for a given $h, k, \bar{h} + \bar{k}$.

† Sulfur atom is replaced by iodine atom.

is obtained when estimates are assigned to invariants associated with the largest product of structure-factor magnitudes rather than to the average of all eight invariants associated with a given triple product of magnitude differences. Table 2 also shows that the average error for invariants composed from acentric reflections remains quite small as the number of data, *i.e.* the number of independent structure-factor magnitudes in P (or PH) used for the calculation, decreases, rising somewhat only when the number of data is reduced to 412. The examples given in Tables 1 and 2 are just a small sample of the thousands of triplet phase invariants that are accessible to evaluation in these relatively simple test structures.

An additional test of R_{iso} may be derived from Table 2 of Hauptman, Potter & Weeks (1982). This table lists results of estimates, based on probability theory, for triplet phase invariants generated by an isomorphous pair involving cytochrome 550. It also lists the six normalized structure-factor magnitudes associated with each triplet phase invariant evaluated for the isomorphous pair. There is good correspondence here between the relative values of normalized structure factors and those of structure factors, although it is not perfect because the scale factor for forming normalized structure factors for the structure labeled PH is not the same as that for P . If this point is ignored and the normalized structure factors, as given, are substituted for the structure factors in applying R_{iso} to Table 2 of Hauptman *et al.* (1982), it is seen that R_{iso} applies without exception to the sample of 50 invariants that are listed.

Concluding remarks

In view of the potential for determining the values of triplet phase invariants by probability methods and

R_{iso} , it is reasonable to inquire how this may affect procedures for phase determination based on the isomorphous-replacement technique. Those invariants that may be known exactly because they are made up of centric reflections are immediately available for phase determination and phase refinement. In addition, general triplet phase invariants whose values are known with some uncertainty may be used in procedures for phase refinement involving the tangent formula or least squares. It would appear that, for instances as complex as macromolecules, the uncertainties associated with the values of the invariants could very well interfere with carrying out a stepwise phase-determination procedure comparable to that used for small structures.

Besides questions associated with the added uncertainties in the value of triplet phase invariants that arise from experimental error, there is another matter of considerable importance that ought to be considered before formulating strategies for application of the theoretical developments. It concerns the fact that the collection of isomorphous-replacement data is usually associated with definitive anomalous dispersion effects. Anomalous dispersion data can add greatly to analytical facility. The technique has a long history of application (Ramaseshan & Abrahams, 1975). The many established procedures for using isomorphous replacement and anomalous dispersion data and newer theoretical developments, that have not yet been applied, such as an exact algebraic analysis of multiwavelength anomalous dispersion experiments (Karle, 1980) and estimates of triplet phase invariants from anomalous dispersion data (Heinerman, Krabbendam, Kroon & Spek, 1978; Hauptman, 1982*b*; Karle, 1983), should all be taken into account in formulating new strategies for phase determination. The recent developments in experimental techniques associated with synchrotron radiation such as, for example, large anomalous

Table 2. *Estimates of values of triplet phase invariants from isomorphous replacement based on isomorphous pair formed from replacement of a sulfur and an oxygen atom by 2 Mg atoms in quinidine sulfate and the absence of both atoms*

Type of invariant	Number of data	Number of invariants	Estimate	Actual average value	Invariant selection*	Average error (rad)
Acentric	2354	64	0	0.02	<i>L</i>	0.29
Acentric	2354	36	π	3.08	<i>L</i>	0.30
Acentric	2354	64($\times 8$)	0	-0.04	<i>A</i>	0.48
Acentric	2354	36($\times 8$)	π	3.07	<i>A</i>	0.59
Acentric	1994	64	0	0.03	<i>L</i>	0.30
Acentric	1994	36	π	3.09	<i>L</i>	0.31
Acentric	806	64	0	0.02	<i>L</i>	0.30
Acentric	806	36	π	3.13	<i>L</i>	0.31
Acentric	412	63	0	0.15	<i>L</i>	0.48
Acentric	412	37	π	3.10	<i>L</i>	0.56
Centric	137	61($\times 8$)	0	0.00	<i>A</i>	0.00
Centric	137	39($\times 8$)	π	3.14	<i>A</i>	0.00

* See Table 1.

dispersion effects for cesium and a number of other heavy atoms at the L_{III} absorption edge (Phillips, Templeton, Templeton & Hodgson, 1978), the virtue of taking advantage of even small effects in anomalous dispersion (Hendrickson & Teeter, 1981) and apparatus for making simultaneous measurements of anomalous dispersion over a range of wavelengths (Arndt, Greenhough, Helliwell, Howard, Rule & Thompson, 1982), combined with the advancing theoretical results, will provide a broad range of opportunities to test and develop optimal procedures.

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The Symmetry of Convergent-Beam Electron Diffraction Patterns from Bicrystals

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Abstract

A discussion of the relationship between the symmetry of bicrystals and the resulting symmetry of convergent-beam electron diffraction (CBED) patterns is presented. For this purpose bicrystal symmetry is defined from the symmetry of the dichromatic pattern or complex formed by the interpenetrating lattices or structures of the individual crystals in a bicrystal. The interrelation between the possible coloured point groups and the diffraction groups, characterizing the symmetry of a CBED pattern, is established. These results are illustrated by a determination of the symmetry of thin twinned Au crystals from suitable CBED patterns. These experiments give information about the state of relative translation of the two crystals at the grain boundary and are consistent with the state of zero translation expected for a (111) coherent twin

boundary in Au. It is pointed out that the interpretation of the CBED pattern symmetry may be complicated by a non-ideal location of the boundary plane in a bicrystal.

1. Introduction

It is now well established that the symmetry of single crystals may be determined in a reliable manner using the technique of convergent-beam electron diffraction (CBED). The relation between the symmetry of CBED patterns and crystal symmetry has been discussed by several authors (Goodman, 1975; Tinnappel, 1975; Buxton, Eades, Steeds & Rackham, 1976). In particular, Buxton *et al.* (1976) have presented a systematic classification of the symmetry of CBED patterns in terms of 31 diffraction groups, which is a very useful tool for crystal symmetry determination.

This paper is concerned with the application of

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