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# The Application of Phase Relationships to Complex Structures
## III. The Optimum Use of Phase Relationships

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An improvement is described in the automatic procedure for solving crystal structures incorporated in the computer program *LSAM*. The development of signs from an initial set containing symbols is carried only as far as is necessary to establish strong relationships between the symbols. The information so gained is used in a fresh beginning of the symbolic-addition process. Some failure of relationships between symbols is allowed to give a multisolution method. A phase-permutation computer program for non-centrosymmetric structures, *MULTAN*, incorporates a weighted tangent formula. This is of the form

$$\tan \varphi_{\mathbf{h}} = \frac{\sum_{\mathbf{h}'} w_{\mathbf{h}'} w_{\mathbf{h}-\mathbf{h}'} \, |E_{\mathbf{h}'} E_{\mathbf{h}-\mathbf{h}'}| \sin (\varphi_{\mathbf{h}'} + \varphi_{\mathbf{h}-\mathbf{h}'})}{\sum_{\mathbf{h}'} w_{\mathbf{h}'} w_{\mathbf{h}-\mathbf{h}'} \, |E_{\mathbf{h}'} E_{\mathbf{h}-\mathbf{h}'}| \cos (\varphi_{\mathbf{h}'} + \varphi_{\mathbf{h}-\mathbf{h}'})} = \frac{T_{\mathbf{h}}}{B_{\mathbf{h}}}$$

and

$$w_{\mathbf{h}} = \tanh\{\sigma_3 \sigma_2^{-3/2} \, |E_{\mathbf{h}}| \, (T_{\mathbf{h}}^2 + B_{\mathbf{h}}^2)^{1/2}\} \, .$$

All phases are accepted as soon as they are found with the associated weight. This gives a fourfold increase in speed in development of the complete phase set. An absolute figure of merit is described to indicate probably correct phase sets for multisolution methods.

Direct methods have now advanced to the point where it can be claimed, with some justification, that they are the major crystallographic tool for the solution of equal-atom structures. There are regularly reported the routine solutions of structures which, not many years ago, would have been regarded as veritable tours de force. However the very efficiency of these methods can lead to a lack of sophistication in their use since even the crudest techniques of application produce results comparable with those of quite intricate alternative methods.

The general philosophy of our approach is to stretch the usefulness of direct methods as far as possible. They are not to be regarded just as an easy alternative to solving structures in some other way but rather as having the potentiality of development to the point where they can solve structures which could not otherwise reasonably be solved. It turns out that there are good and bad ways of using any given data set and that with the right techniques structures can be solved which do not yield to the most obvious methods of applying sign and phase relationships. We shall here describe the methods which we have found to be the most effective and to have given solutions when other methods have failed.

### Centrosymmetric structures

The multisolution symbolic-addition process for centrosymmetric structures described by Germain & Woolfson (1968) has been fully automated in the *LSAM* (Logical Symbolic Addition Method) computer program. The program goes through the stages:

(I) There are allocated origin-fixing signs to some reflexions and sign symbols to up to six others.

(II) From the $\sum_2$ relationship there is found the reflexion whose sign (perhaps in symbolic form) is given with the highest probability. This is added to the list of known signs and the process repeated until the highest probability is lower than some preset limit, $P_L$.

(III) All the triple-product sign relationships involving reflexions in the known list are examined to find relationships between sign symbols.

(IV) All sets of signs for symbols are found which satisfy a specified number of the strongest relationships between sign symbols. Each of these sets constitutes a possible solution.

(V) For each possible set of signs various figures of merit are computed which normally enable the correct solution to be recognized.

Relationships between sign symbols, found at stage III, are related to the situation in stage II when a reflexion is found in terms of two different combinations of symbols. Thus a reflexion may have an indicated sign

$$\begin{array}{ll} & AB \text{ with probability } 0{\cdot}90 \\ \text{and} & CD \text{ with probability } 0{\cdot}85\,. \end{array} \qquad (1)$$

If 0·90 is greater than $P_L$ and is the highest probability for any new sign indication at this stage then the

Table 1. *Computer output for the sign determining process*

```
                     2,3,4,5 TETRAPHENYLCYCLCPENTACIENE                  10 JULY 1969

PRCBABILITY LIMIT FOR ACCEPTANCE OF SIGN SYMBOL IS   .9500

NUMBER CF SIGNS CETERMINED IS   86

   SYMBOL         A         B         C         D         E         F

FRECUENCY        29        53        33         0         0         0


   1    A 1.CC00         2    B 1.0000         3  ABC 1.C000         4   BC 1.0000         5    B -.0000
   6   BC  .CC00         7    C  .9358         8    C 1.C000         9        .5000        10   AB 1.0000
  11   AB  .2075        12        .5CC0        13        .5000        14    B 1.C000        15    + 1.0000
  16    B -.CCC0        17        .5CCC        18   BC  .9993        19  ABC  .9999        20        .5C00
  21        .5C00        22   AC 1.0000        23        .5000        24        .5000        25    C 1.0000
  26    + 1.CC00        27   AB 1.C0CC        28    +  .1824        29        .5000        30        .5000
  31    + 1.CC00        32    B 1.C0C0        33    B 1.0000        34  ABC  .1854        35   BC -.0000
  36   BC  .9999        37   BC 1.CCC0        38        .5CC0        39        .5C00        40   BC  .0457
  41        .5C00        42    B  .0000        43    B  .6857        44        .5C00        45   BC  .0731
  46   AB 1.CC00        47   AC  .2315        48        .5000        49    + 1.C000        50        .5000
  51        .5C00        52        .5C00        53        .5000        54        .5C00        55        .5000
  56   AB  .9998        57        .5CC0        58    C  .0019        59    A  .3186        60        .5000
  61        .5C00        62   AB 1.0CC0        63   BC  .0011        64        .5000        65  ABC  .9153
  66        .5C00        67        .5C00        68    C 1.C000        69    C  .8402        70        .5000
  71        .5CC0        72        .5CC0        73   AB  .0802        74    B  .9993        75    +  .9996
  76   BC  .0C04        77        .5CCC        78    B  .9999        79        .5000        80   AB  .0023
  81   BC  .00C0        82        .5C00        83        .5000        84    +  .9999        85    B 1.0000
  86    C 1.CCC0        87   BC  .3274        88   AB  .7685        89    A  .1016        90        .5000
  91   AB  .0CC0        92        .5CC0        93    +  .C000        94   BC  .9999        95   BC  .9996
  96        .5C00        97   BC  .2769        98        .5000        99    C  .1371       100    B  .9999
 101   AB  .9997       102    A  .2650       103        .5000       104        .5000       105   AB  .4750
 106    B 1.CC00       1C7   BC  .3498       108        .5000       109   AB  .7577       110  ABC 1.0000
 111   AB  .3498       112  ABC  .9988       113        .5000       114  ABC  .9958       115   AB  .0595
 116    C  .9997       117    B  .411C       118        .5000       119        .5000       120    B  .3823
 121   BC  .3870       122  ABC  .9296       123    B  .1347       124   AC  .7271       125        .5000
 126        .50C0       127        .5CC0       128   AB  .9974       129    C  .9994       130   AC  .0054
 131    B  .0431       132        .5000       133   AB 1.C000       134    +  .9988       135    C  .0002
 136        .5C00       137    A  .7858       138    B  .0006       139    A  .0034       140    +  .0124
 141    +  .0044       142        .5CC0       143        .5000       144        .5000       145    B  .7721
 146    +  .0058       147        .5CC0       148        .50C0       149    B  .2973       150        .5000
 151        .50C0       152    C  .8085       153  ABC  .C215       154    +  .0131       155    B  .0000
 156    +  .0552       157        .5000       158        .5000       159        .5000       160    +  .2423
 161   AC  .0522       162        .5CC0       163        .5000       164    +  .8205       165        .5C00
 166        .5CC0       167        .5CC0       168    B  .3318       169        .5000       170    C  .4061
 171    +  .99C0       172        .50C0       173    C  .9949       174    C  .7858       175        .5C00
 176    B  .3870       177        .5000       178        .5000       179        .5000       180        .5000
 181   AC  .8264       182    B  .0017       183        .500C       184    +  .0000       185        .5000
 186  ABC  .3965       187    B  .9405       188        .5000       189  ABC  .6770       190    B  .6130
 191    C  .5987       192   BC  .9945       193   AB  .998C       194        .5C00       195    + 1.0000
 196    B  .2689       197        .5000       198        .5000       199        .5000       200        .5000
 201        .5C00       202   BC  .8870       203        .5000       204        .5000       205        .5C00
 206    B  .9468       207        .5CC0       208    B  .9965       209        .5000       210    B  .1347
 211        .5000       212        .5CC0       213        .5000       214        .5C00       215   AB  .5890
 216        .5C00       217        .50C0       218        .5000       219        .5000       220    A  .9999
 221        .5C00       222        .5CC0       223   BC  .4158       224        .5000       225        .5000
 226        .5C00       227        .5000       228   AC  .7311       229        .5000       230        .5000
 231    A  .9999       232        .5CC0       233        .5000       234        .5000       235        .5000
 236        .5000       237   BC  .9437       238        .5000       239   BC  .3274       240        .5000

 241        .5C00       242        .5CCC       243        .5000       244        .5000       245        .5000
 246    +  .2244       247   BC  .5987       248        .5000       249   AB  .7427       250    B  .7649
 251        .5C0C       252    B  .4651       253        .5000       254        .5000       255        .5000
 256    B  .7388       257        .5CC0       258        .5000       259        .5000       260        .5C00
 261   AC  .1493       262        .5CC0       263    C  .7311       264   BC  .2932       265    B  .9072
 266        .5C00       267        .5C00       268    A  .6593       269    +  .3100       270   AB  .9658
 271        .5C00       272        .5000       273        .5000       274        .5000       275        .5000
 276        .5C00       277        .5CC0       278        .5000       279   AC  .7427       280        .5000
 281   BC  .8455       282        .5CC0       283        .5000       284        .5000       285        .5000
 286        .5C00       287    B  .0035       288   BC  .9072       289        .5C00       290    B  .1545
 291        .5C00       292        .5000       293    B  .7503       294        .5000       295        .5000
 296        .5C00       297    +  .5890       298        .5000       299        .5000       300   AB  .3635
 301    B  .2176       302        .5CC0       303   AB  .9866       304   AB  .7388       305        .5000
 306    +  .9689       307    B  .2891       308   BC  .6271       309  ABC  .9623       310        .5000
 311        .5C00       312        .5000       313        .5000       314        .5000       315    B  .6365
 316        .5C00       317   AB  .3498       318    C  .7068       319        .5000       320    B  .9346
 321    B  .0847       322        .5000       323    B  .4061       324    B  .2315       325   BC  .6457
 326    C  .9998       327    B  .8375       328   AB  .9593       329        .5C00       330   AB  .4013
 331   AB  .9282       332    +  .1347       333        .5000       334        .5000       335   BC  .7311
 336   BC  .6225       337        .5CC0       338  ABC  .6548       339        .5000       340        .5000
 341        .5CC0       342        .5C00       343   BC  .2729       344        .5000       345        .5000
 346    A  .6857       347        .5CCC       348        .5000       349        .5000       350        .5000
 351        .5000       352   AC  .9967       353        .5000       354        .5000       355        .5000
 356   BC  .1571       357   AB  .6271       358    B  .2891       359    B  .0563       360   AC  .0911
 361        .5C00       362   BC  .2932       363        .5000       364    A  .6900       365        .5000
 366        .5C00       367   BC  .5939       368        .5000       369        .5000       370        .5000
 371    C  .3870       372        .5000       373        .5000       374        .5000       375        .5000
 376        .5C00       377    A  .3635       378    C  .6411       379        .5000       380        .5000
 381    B  .7649       382        .5C00       383   AB  .9969       384        .5C00       385    B  .8115
 386        .5C00       387        .5CC0       388        .5000       389        .5000       390   AB  .3917
 391  ABC  .9241       392        .5000       393    C  .1765       389        .5000       390   AB  .3917


                     2,3,4,5 TETRAPHENYLCYCLCPENTACIENE                  10 JULY 1969

          RELATICNSHIPS BETWEEN SYMBOLS

                                 RELATICNSHIP          PRCBABILITY

                                   AC = S( 1)            -.0C0C
                                    A = S( 2)            1.CCCC
                                    C = S( 3)             .0001
```

symbol $AB$ will be accepted for this reflexion. Subsequently at stage III there will be a relationship between symbols

$$ABCD \simeq +1 .$$

In practice, for reasonably complex structures, to get most reflexions determined in terms of symbols, $P_L$ must be made as low as about 0·80. If several sign indications are accepted at this level of probability there is a non-negligible likelihood that some of them may be wrong.

There is another aspect of this situation which can be seen from the example given in (1). If $AB$ and $CD$ are actually similar sign indications, *i.e.* both plus or both minus, with probabilities $P_1$ and $P_2$ then the actual probability that the new sign indication is $AB$ (or $CD$) is

$$P = \frac{P_1P_2}{1-P_1-P_2+2P_1P_2} . \tag{2}$$

For the numerical values quoted this gives $P=0{\cdot}98$, a very high probability. However if $AB$ and $CD$ are actually opposite indications then the resultant probability for the sign being $AB$ is only 0·61. In this event the chance of error is high and if prior knowledge of the signs represented by $A$, $B$, $C$ and $D$ was available the next reflexion to have its sign accepted would certainly not be this one.

The *LSAM* program in its original form has only once failed to solve a structure in such a way that the best set of signs gave an easily recognizable and substantially correct Fourier map. This was for the structure 2,3,4,5-tetraphenylcyclopentadiene, space group $C2/c$ with eight molecules in the unit cell. The *LSAM* program produced seven sets of signs; the map from the set with the highest figures of merit gave a recognizable molecule in a location which was obviously incorrect from packing considerations. The structure was eventually solved by a process which involved relaxing the space group to $C2$ (Evrard, 1971). When the *LSAM* determined signs were compared with those from the refined structure it was found that about one-third of them had been incorrect.

A '*post mortem*' on this structure suggested that at some fairly early stage in sign development a wrong indication had been accepted. From this investigation there emerged a revision of the sign-development technique which is incorporated in the latest version of the program, *LSAM* 2.

In applying *LSAM* 2 to 2,3,4,5-tetraphenylcyclopentadiene, 393 reflexions with $E>1{\cdot}5$ were utilized. The program selected two reflexions to fix the origin (space group $C2/c$) and three others to which it allocated letter symbols $A$, $B$ and $C$. New signs were generated as in stage II but with a high probability limit, $P_L=0{\cdot}95$. This caused the sign determining process to terminate with 86 signs developed. In Table 1 the computer output is shown at this stage. It is to be interpreted as follows: reflexion 36 has sign $BC$ with probability 0·9999 while reflexion 131 has sign $-B$ with probability 0·9569. Where the probability of an indication is less than 0·95 that reflexion has not been used in $\sum_2$ relationships to deduce extra signs.

The program next searched for relationships between symbols and found three

$$AC=-1, \text{ probability } 1{\cdot}0000$$
$$A=+1, \text{ probability } 0{\cdot}9999$$
and
$$C=-1, \text{ probability } 0{\cdot}9998 .$$

These are shown at the foot of Table 1.

We see from this that to get strong relationships between symbols does not require the development of signs for most of the reflexions and that one can insist on much higher probabilities up to this stage. *LSAM* next considered the possibilities

$$A=+1 , \quad B=+1 , \quad C=-1$$
and
$$A=+1 , \quad B=-1 , \quad C=-1$$

and started again from the beginning developing signs for each combination. The output from this stage is shown in Table 2. The second set had the higher figures of merit (Germain & Woolfson, 1968) and of the 372 signs determined in this set only 3 were incorrect. In fact *LSAM* was prepared to allow other combinations of sign for $A$, $B$ and $C$ – up to six in all – but the operator intervened so only the two most probable ones were considered.

It is possible to deduce why the change of procedure gave a successful outcome in this case. If it is assumed that the relationships from which the initial 86 signs were determined were all independent then the probability that all these signs were determined without error was the product of the individual probabilities for each sign being correct. This gives $P_+$ equal to about 0·70 and it is therefore more likely that all the signs are correctly found than that there should be any error. The true value of $P_+$ is higher since it is known that probabilities given by the usual hyperbolic tangent formula are an underestimate (Klug, 1958); while this is usually of little importance when considering the validity of a single sign determination it is more significant in this case where 86 probabilities are being multiplied together.

If the original scheme, when signs were developed by a step by step process with $P_L=0{\cdot}80$, is examined in the same way then it is found that some incorrect sign determinations are almost inevitable. With, say the 100th sign incorrectly determined experience suggests that the situation would soon deteriorate to the point where from about the 150th sign onwards completely random signs might be generated. Relationships between sign symbols deduced from the total resultant sign determination would be rather uncertain and there would thus be a high likelihood of failure.

This analysis also suggests an objective procedure as an alternative to initially fixing a value of $P_L$ by judg-

Table 2. *Computer output for the development of signs for combinations of* $A, B, C = \pm 1$

The two most-probable combinations are shown.

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                         LSAH    PART 2          GERPAIN/PAIN  VERSION  JUNE  1969

                      2,3,4,5 TETRAPFENYLCYCLCPENTACIENE                      10 JULY 1969

THE FIRST  3 ECUATIONS TO EE CONSIDEREC

TPE SCLUTICN IS
                    A B C D E F      S( 1) S( 2) S( 0) S( 0) S( 0) S( 0)  SIGN

              A  =  0 0 0 0 C 0        C     1     C     0     0     0     1
              B  =  0 1 0 0 C 0        0     0     0     0     0     0     1
              C  =  C 0 C C C 0        1     1     0     0     0     0    -1
              D  =  C 0 0 0 C 0        0     0     0     0     0     0     0
              E  =  0 0 0 0 C 0        0     0     C     0     0     0     0
              F  =  0 0 0 0 0 0        0     0     0     0     0     0     0

NUPBER   CF   SYPECLS   SCLVEC   FOR   IS      2

NUPBER CF SETS CF SIGNS TO EE GENERATED IS     6

SIGN ACCEPTEC IF PRCBABILITY GREATER TFAN   .80C


SET NC  1           SIGNS OF SYMBOLS   + + - + + +        FIGURES OF MERIT      1099.5    1353.4    1490     371

       1  +      2  +      3  -      4  -      5  -      6  +      7  -      8  -      9  +     10  +
      11  -     12  -     13  +     14  +     15  +     16  -     17  -     18  -     19  -     20  -
      21  +     22  -     23  +     24  -     25  -     26  +     27  +     28  -     29  -     30  +
      31  +     32  +     33  +     34  +     35  +     36  -     37  -     38  -     39  +     40  +
      41  -     42  -     43  -     44  -     45  +     46  +     47  +     48  +     49  +     50  -
      51  +     52  +     53  +     54  -     55  +     56  +     57  -     58  +     59  -     60  +
      61  +     62  +     63  +     64  -     65  -     66  +     67  -     68  -     69  +     70  -
      71  +     72  -     73  -     74  +     75  +     76  +     77  -     78  +     79  +     80  -
      81  +     82  -     83  +     84  +     85  +     86  -     87  +     88  +     89  -     90  +
      91  -     92  +     93  -     94  -     95  -     96  -     97  -     98  +     99  +    100  +
     101  +    102  -    103  +    104  +    105  -    106  +    107  +    108  -    109  +    110  -
     111  -    112  -    113  -    114  -    115  -    116  -    117  +    118  +    119  -    120  +
     121  -    122  -    123  -    124  -    125  -    126  -    127  +    128  +    129  -    130  +
     131  +    132  +    133  +    134  +    135  +    136  -    137  +    138  -    139  -    140  -
     141  -    142  -    143  +    144  +    145  +    146  -    147  -    148  +    149  +    150  -

     151  +    152  -    153  +    154  -    155  -    156  +    157  +    158  +    159  +    160  -
     161  +    162  +    163  +    164  +    165  -    166  -    167  r    168  +    169  -    170  +
     171  +    172  +    173  -    174  +    175  +    176  +    177  +    178  +    179  -    180  +
     181  -    182  -    183  -    184  -    185  -    186  +    187  +    188       189  -    190  +
     191  +    192  -    193  +    194  +    195  +    196  +    197  -    198  -    199  +    200  -
     201  +    202  -    203       204  -    205  +    206  +    207  +    208  +    209       210  -
     211  -    212       213  +    214       215  -    216       217       218  +    219       220  +
     221  +    222  -    223  +    224       225  -    226       227  +    228  -    229  -    230
     231  +    232  -    233       234       235  -    236  -    237  -    238       239  +    240
     241       242       243  +    244       245       246  -    247  +    248  -    249  +    250  -
     251  -    252  -    253  +    254  +    255  -    256  +    257  +    258  -    259  -    260  +
     261  +    262  -    263  -    264  +    265  +    266  -    267  +    268  -    269  -    270  +
     271  +    272  -    273       274  -    275  -    276  -    277  -    278  +    279  -    280  +
     281  -    282  -    283  +    284  +    285  +    286  -    287  -    288  -    289  -    290  -
     291  -    292  +    293  +    294  -    295  +    296  -    297  +    298  -    299  -    300
     301  -    302  +    303  +    304  +    305  -    306  +    307  -    308  -    309  -    310  -
     311  +    312  +    313  -    314  +    315  +    316  +    317  -    318  -    319  +    320  +
     321  -    322  -    323  -    324  +    325  -    326  -    327  +    328  +    329  +    330  -
     331  +    332  +    333  +    334  -    335  -    336  -    337  +    338  -    339  -    340  -
     341  +    342  +    343  +    344  +    345  +    346  -    347  +    348  -    349  -    350  +
     351  +    352  -    353  +    354  +    355       356  +    357  +    358  +    359  -    360  +
     361  -    362  -    363  -    364  -    365  -    366  +    367  -    368  +    369  +    370  -
     371  -    372  -    373  -    374  +    375  +    376  +    377  +    378  -    379  +    380  -
     381  +    382  -    383  +    384  +    385  +    386  -    387  -    388  +    389  -    390  -
     391  -    392  -    393  -


SET NC  2           SIGNS OF SYMBOLS   + - - + + +        FIGURES OF MERIT      1251.9    1506.1    1592     374

       1  +      2  -      3  +      4  +      5  +      6  -      7  -      8  -      9  -     10  -
      11  +     12  +     13  -     14  -     15  +     16  +     17  +     18  +     19  +     20  +
      21  -     22  -     23  -     24  +     25  -     26  +     27  -     28  -     29  +     30  -
      31  +     32  -     33  -     34  -     35  -     36  +     37  +     38  +     39  -     40  -
      41  +     42  +     43  +     44  +     45  -     46  -     47  +     48  -     49  +     50  +
      51  -     52  +     53  -     54  -     55  +     56  -     57  +     58  +     59  -     60  +
      61  +     62  -     63  -     64  +     65  +     66  +     67  +     68  -     69  +     70  +
      71  -     72  -     73  +     74  -     75  +     76  -     77  -     78  -     79  -     80  +
      81  -     82  -     83  +     84  +     85  -     86  -     87  -     88  -     89  -     90  +
      91  +     92  -     93  -     94  +     95  +     96  -     97  +     98  -     99  +    100  -
     101  -    102  -    103  +    104  +    105  +    106  -    107  -    108  -    109  -    110  +
     111  +    112  +    113  +    114  +    115  +    116  -    117  -    118  +    119  +    120  -
     121  +    122  +    123  +    124  -    125  -    126  +    127  -    128  -    129  -    130  +
     131  -    132  +    133  -    134  +    135  +    136  +    137  +    138  +    139  -    140  -
     141  -    142  +    143  +    144  +    145  -    146  -    147  +    148  +    149  -    150  +
     151  -    152  -    153  -    154  -    155  +    156  +    157  -    158  +    159  -    160  -
     161  +    162  -    163  -    164  +    165  -    166  +    167  +    168  -    169  -    170  -
     171  +    172  -    173  -    174  +    175  -    176  -    177  -    178  +    179  +    180  +
     181  -    182  +    183  +    184  -    185  +    186  -    187  -    188       189  +    190  -
     191  +    192  +    193  -    194  -    195  .    196  -    197  +    198  +    199  -    200  +
     201  +    202  +    203       204  +    205  +    206  -    207  -    208  -    209       210  +
     211  +    212       213  -    214       215  -    216       217       218  -    219  .    220  +
     221  +    222  +    223  -    224       225  +    226       227  +    228  -    229  +    230
     231  +    232  +    233       234       235  -    236  +    237  +    238       239  -    240
     241       242       243  +    244       245       246  -    247  -    248  +    249  -    250  +
     251  +    252  +    253  -    254  +    255  +    256  -    257  -    258  -    259  -    260  -
     261  +    262  +    263  -    264  -    265  -    266  +    267  +    268  -    269  -    270  -
     271  -    272  -    273  +    274  -    275  -    276  +    277  -    278  -    279  -    280  +
     281  +    282  +    283  -    284  -    285  -    286  -    287  +    288  +    289  -    290  +
     291  +    292  -    293  -    294  +    295  +    296  +    297  +    298  +    299  -    300  -

     301  +    302  +    303  -    304  -    305  +    306  +    307  +    308  +    309  +    310  +
     311  +    312  +    313  -    314  -    315  -    316  -    317  +    318  -    319  +    320  -
     321  +    322  -    323  +    324  -    325  +    326  -    327  -    328  -    329  -    330  +
     331  -    332  +    333  -    334  +    335  +    336  +    337  -    338  +    339  +    340  +
     341  +    342  -    343  -    344  +    345  +    346  -    347  -    348  -    349  -    350  -
     351  +    352  -    353  +    354  -    355  +    356  -    357  -    358  -    359  +    360  +
     361  +    362  +    363  +    364  -    365  -    366  +    367  +    368  -    369  +    370  +
     371  -    372  +    373  +    374  +    375  +    376  +    377  +    378  -    379  +    380  -
     381  -    382  -    383  -    384  +    385  -    386  +    387  +    388  -    389  +    390  +
     391  +    392  +    393  -
```

ment. One may begin by finding new signs, one at a time, and calculating the cumulative product of probabilities at each step. When this has reached some value, 0·95 for example, all possible relationships between symbols can be found and if the probabilities of these are judged to be high enough then stage IV of the process can be commenced. Otherwise one goes further in finding new signs until the cumulative product has reached another limit, say 0·90. The search process is continued until the probability of the cumulative product is as high as possible compatible with having sufficiently high probabilities for the relationships between symbols. This procedure is not written into *LSAM* at the time of writing but may be included in due course.

### Non-centrosymmetric structures

The multi-solution method of solving crystal structures proposed by Germain & Woolfson (1968) has been fully automated in the *MULTAN* computer program and a number of fairly complex structures (up to 46 atoms in the asymmetric unit, $P2_12_12_1$) have been solved in this way.

Various trial procedures for phase development have been tried. They all had the general character that the strongest new phase indication from the tangent formula was accepted and incorporated in the known set and that after $n$ such new phase determinations cyclic refinement of phases by the tangent formula was carried out. The various techniques tried were:

(1) Taking $n$ small, about five to ten, so that one always went forward with a highly self-consistent set of phases.
(2) Taking $n$ very large so that new phases were accepted in large numbers before refinement was carried out.
(3) Making successive values of $n$ increase in some exponential way, *i.e.* 5, 10, 20, 40 *etc.*

The trials showed, rather surprisingly, that frequent refinement was not only time-consuming but could be positively harmful. For example in one trial with space group $P2_12_12_1$ and 142 reflexions the starting set contained seven reflexions. With $n=10$ the final mean error in determined phase angle was 85·2°. For $n=20$ or any higher value up to 135 the mean error in determined phase angle was about 30°!

However the fastest and most efficient process of all was found to be the use of a weighted tangent formula. Whenever a new phase, $\varphi_{\mathbf{h}}$, is determined there is also calculated a corresponding weight, $w_{\mathbf{h}}$. An effective scheme, incorporated in a routine called *FASTAN*, was found to be

$$\tan\varphi_{\mathbf{h}} \simeq \frac{\sum\limits_{\mathbf{h}'} w_{\mathbf{h}'}w_{\mathbf{h}-\mathbf{h}'}|E_{\mathbf{h}'}E_{\mathbf{h}-\mathbf{h}'}|\sin(\varphi_{\mathbf{h}'}+\varphi_{\mathbf{h}-\mathbf{h}'})}{\sum\limits_{\mathbf{h}'} w_{\mathbf{h}'}w_{\mathbf{h}-\mathbf{h}'}|E_{\mathbf{h}'}E_{\mathbf{h}-\mathbf{h}'}|\cos(\varphi_{\mathbf{h}'}+\varphi_{\mathbf{h}-\mathbf{h}'})} = \frac{T_{\mathbf{h}}}{B_{\mathbf{h}}} \quad (3)$$

$$w_{\mathbf{h}} = \tanh\{\sigma_3\sigma_2^{-3/2}|E_{\mathbf{h}}|(T_{\mathbf{h}}^2+B_{\mathbf{h}}^2)^{1/2}\}\,. \quad (4)$$

where $\sigma_2$ and $\sigma_3$ have been defined by Karle & Karle (1966).

Since the tangent formula is weighted, all reflexions are included the whole of the time and there is no rejection criterion for a phase other than the weight being calculated as very small or zero. The form of weighting ensures that poorly determined phases have little effect in the determination of other phases, while the fact that all phases are included in the phase determination process leads to very efficient propagation of phase knowledge throughout the data set. It has been found that the weighted tangent formula converges on the final result significantly more quickly than the normal unweighted formula where one starts with a small subset of $E$'s and only after several cycles is the whole of the data included. In the authors' own case, the weighted tangent formula is about four times faster than the more conventional approach and on at least one occasion gave the correct structure when the unweighted tangent formula did not.

The weighting scheme, as proposed in equations (3) and (4), is an empirical one which is found to give sensible results. For this, as with most weighting schemes, the important thing is to get the right general form for the weighting function and the exact analytical expression used is normally not very critical.

The final phases as given by *FASTAN* have associated weights and a small weight indicates an uncertain phase. It can be shown by an approximate analysis that, taking these uncertainties into consideration, a Fourier synthesis with suitably weighted coefficients $K|E|$ gives a higher signal:noise ratio than a normal $|E|$ map.

Let us consider a Fourier map

$$\Psi(\mathbf{r}) = \sum_{\mathbf{h}} K_{\mathbf{h}}|E_{\mathbf{h}}|\cos(2\pi\mathbf{h}\,.\,\mathbf{r}-\varphi_{\mathbf{h}}) \quad (5)$$

at $r_j$, the centre of the $j$th atom

$$\Psi(\mathbf{r}_j) = \sum_{\mathbf{h}} K_{\mathbf{h}}|E_{\mathbf{h}}|\cos(2\pi\mathbf{h}\,.\,\mathbf{r}_j-\varphi_{\mathbf{h}})\,. \quad (6)$$

It can be shown by arguments similar to those given by Cochran & Woolfson (1955) that the expectation value of $\cos(2\pi\mathbf{h}\,.\,\mathbf{r}_j-\varphi_{\mathbf{h}})$ is

$$\langle\cos(2\pi\mathbf{h}\,.\,\mathbf{r}_j-\varphi_{\mathbf{h}})\rangle = \frac{Z_j}{\{\sum Z_i^2\}^{1/2}}|E_{\mathbf{h}}| \quad (7)$$

where $Z_j$ is the atomic number of the $j$th atom and the summation is over all atoms in the unit cell. It is assumed in this that the form factors of the various atoms all have the same shape and differ only by a scale factor.

Replacing the cosine in expression (6) by its expectation value we have

$$\langle\Psi(\mathbf{r}_j)\rangle = \frac{Z_j}{\{\sum Z_i^2\}^{1/2}}\sum_{\mathbf{h}} \mathrm{K}_{\mathbf{h}}|\mathrm{E}_{\mathbf{h}}|^2\,. \quad (8)$$

If the errors in $\varphi_{\mathbf{h}}$ are not too large we can obtain an expression for the error in $\Psi(\mathbf{r}_j)$ due to errors in the $\varphi_{\mathbf{h}}$'s. This is

$$\Delta\Psi(\mathbf{r}_j) = -\sum_{\mathbf{h}} K_{\mathbf{h}}|E_{\mathbf{h}}| \sin(2\pi\mathbf{h}\,.\,\mathbf{r}_j - \varphi_{\mathbf{h}})\Delta\varphi_{\mathbf{h}}\,. \tag{9}$$

Since the $\Delta\varphi_{\mathbf{h}}$'s are as equally likely to be positive as negative the expectation value of $\Delta\Psi(\mathbf{r}_j)$ is zero.

However the mean-square value of $\Delta\Psi(\mathbf{r}_j)$ is non-zero and equals

$$\langle\{\Delta\Psi(\mathbf{r}_j)\}^2\rangle = \sum K_{\mathbf{h}}^2|E_{\mathbf{h}}|^2\langle\sin^2(2\pi\mathbf{h}\,.\,\mathbf{r}_j - \varphi_{\mathbf{h}})\Delta\varphi_{\mathbf{h}}^2\rangle\,. \tag{10}$$

Taking

$$\langle\sin^2(2\pi\mathbf{h}\,.\,\mathbf{r}_j - \varphi_{\mathbf{h}})\rangle = 0{\cdot}5$$

and

$$\langle\Delta\varphi_{\mathbf{h}}^2\rangle = V_{\mathbf{h}}$$

the variance in the determination of $\varphi_{\mathbf{h}}$, we find the root-mean-square value of $\Delta\Psi(\mathbf{r}_j)$

$$\langle\{\Delta\Psi(\mathbf{r}_j)\}^2\rangle^{1/2} = \{\tfrac{1}{2}\sum_{\mathbf{h}} K_{\mathbf{h}}^2|E_{\mathbf{h}}|^2V_{\mathbf{h}}\}^{1/2}\,. \tag{11}$$

For a high signal-to-noise ratio we might expect the ratio of the expression given in (8) to that given in (11) to be a maximum *i.e.* ignoring constant factors,

$$X = \frac{\sum_{\mathbf{h}} K_{\mathbf{h}}|E_{\mathbf{h}}|^2}{\left\{\sum_{\mathbf{h}} K_{\mathbf{h}}^2|E_{\mathbf{h}}|^2V_{\mathbf{h}}\right\}^{1/2}}\,. \tag{12}$$

to be a maximum.

Multiplying all the $K$'s by a constant factor does not affect the value of $X$ so we can consider the problem as one of minimizing $\sum_{\mathbf{h}} K_{\mathbf{h}}|E_{\mathbf{h}}|^2V_{\mathbf{h}}$ while keeping $\sum K_{\mathbf{h}}|E_{\mathbf{h}}|^2$ fixed.

Now

$$\mathrm{d}(\sum K_{\mathbf{h}}|E_{\mathbf{h}}|^2) = \sum_{\mathbf{h}}|E_{\mathbf{h}}|^2\mathrm{d}K_{\mathbf{h}} = 0 \text{ for constant } \sum_{\mathbf{h}} K_{\mathbf{h}}|E_{\mathbf{h}}|^2$$

and

$$\mathrm{d}(\sum K_{\mathbf{h}}^2|E_{\mathbf{h}}|^2V_{\mathbf{h}}) = 2\sum_{\mathbf{h}} K_{\mathbf{h}}|E_{\mathbf{h}}|^2V_{\mathbf{h}}\mathrm{d}K_{\mathbf{h}}$$

$$= 0 \text{ for } \sum_{\mathbf{h}} K_{\mathbf{h}}^2|E_{\mathbf{h}}|^2V_{\mathbf{h}} \text{ to be a minimum.}$$

The values of $K_{\mathbf{h}}$ satisfy the second condition if $K_{\mathbf{h}}V_{\mathbf{h}}$ equals a constant.

It is found that if we interpret the quantity

$$\alpha_{\mathbf{h}}' = 2\sigma_3\sigma_2^{-3/2}|E_{\mathbf{h}}|(T_{\mathbf{h}}^2 + B_{\mathbf{h}}^2)^{1/2} \tag{13}$$

which is twice the argument of tanh in equation (4), as corresponding to the normal $\alpha_{\mathbf{h}}$ as defined by Karle & Karle (1966) then $K_{\mathbf{h}} = \alpha_{\mathbf{h}}$ is a reasonable approximation. This is shown in Table 3; the values of $\alpha$ and $V$ may be found tabulated in the paper by Germain, Main & Woolfson (1970).

Table 3. *Values of $\alpha$, $V$ and $\alpha V$*

| $\alpha$ | $V$ (radians$^2$) | $\alpha V$ (radians$^2$) | $\alpha$ | $V$ (radians$^2$) | $\alpha V$ (radians$^2$) |
|---|---|---|---|---|---|
| 0·0 | 3·290 | 0.000 | 6·0 | 0·184 | 1·104 |
| 0·5 | 2·349 | 1·175 | 8·0 | 0·134 | 1·072 |
| 1·0 | 1·604 | 1·604 | 10·0 | 0·106 | 1·060 |
| 2·0 | 0·764 | 1·528 | 12·0 | 0·087 | 1·044 |
| 3·0 | 0·437 | 1·311 | 16·0 | 0·065 | 1·040 |
| 4·0 | 0·298 | 1·192 | 20·0 | 0·051 | 1·020 |

The values of $\alpha_{\mathbf{h}}'$, which vary between 0·6 and 56·9, are shown as ALPHA in Table 4 which is a typical output from *FASTAN* for a trial structure.

The above rough analysis suggests that $\alpha_{\mathbf{h}}'|E_{\mathbf{h}}|$ should be used as a Fourier coefficient to get the greatest signal-to-noise ratio. However this analysis is rather rough and the derivation of equation (9) depends on small errors in the $\varphi$'s – which will not always be the case. The authors feel that weighting according to $\alpha_{\mathbf{h}}'$ is possibly too severe and that instead $w_{\mathbf{h}}$ may turn out to be a more sensible weighting function. For the extreme values of $\alpha_{\mathbf{h}}'$ of 0·6 and 56·9 the corresponding values of $w_{\mathbf{h}}$ are 0·291 and 1·000. Further investigations of weighting, both theoretical and empirical, will be made in due course.

## Additional information

Germain, Main & Woolfson (1970) described the convergence method for selecting origin-and-enantiomorph-fixing reflexions together with some others to form a good starting set. As described in that paper the investigator chose origin-and-enantiomorph-fixing reflexions and these were tested for efficiency by the convergence method which also found the best other reflexions to take with them.

An improved version of the convergence method is incorporated in *MULTAN* as a routine called *CONVERGE.* This does not require any intervention on the part of the investigator but automatically finds the best possible starting set of reflexions including those required to fix the origin and enantiomorph.

The routine *CONVERGE* also applies the $\sum_1$ formula (Hauptman & Karle, 1953) to find probable signs of centric reflexions. The form of the $\sum_1$ expressions depends on the space group; for $P2_12_12_1$ for example one finds

$$S\{E_{2h2k0}\} \simeq S\{\sum_l(-1)^{l+h}(|E^{hkl}|^2 - 1)\} \tag{14}$$

with the probability that $E_{2h,2k,0}$ is positive

$$P_+\{E_{2h2k0}\} = \tfrac{1}{2} + \tfrac{1}{2}\tanh\{\tfrac{1}{2}\sigma_3\sigma_2^{-3/2}|E_{2h,2k,0}| \times \sum_l(-1)^{l+h}(|E_{hkl}|^2 - 1)\}\,. \tag{15}$$

The weight associated with each sign determination is $|2P-1|$ (see, for example, Woolfson, 1956) and $\sum_1$

phases with these weights can be incorporated into the starting sets. Their phases are kept constant and contribute to the phase determination with their initial weight until they are determined by the tangent formula with a larger weight. Thereafter they take on the value and weight indicated by the tangent formula. The other reflexions in the starting set are kept constant until the tangent formula refinement has essentially converged; they are then allowed to refine to their final values which takes about two further cycles.

In Table 5 is shown the beginning and end of the output from *CONVERGE*. There were six signs found from $\sum_1$ and these were all included in the starting set. Although one of them (10,0,8) was incorrect the weighting scheme was able to handle the situation and a correct set of phases was found. There were two general phases whose phases were permuted in various combinations of $\pm(\pi/4 \text{ or } 3\pi/4)$ giving sixteen different starting points to be explored.

*MULTAN* gives a number of possible sets of phases and in order to evaluate their relative plausibility it is necessary to have some figures of merit. One fairly obvious criterion is

$$Z = \sum_{\mathbf{h}} \alpha_{\mathbf{h}} \tag{16}$$

and it appears that it often enables the correct solution to be distinguished from incorrect solutions. However it is difficult to judge the worthiness of the values of $Z$ in an absolute way – that is to say that one cannot tell whether or not the highest value of $Z$ might conceivably correspond to a correct solution. For this reason we have developed an absolute figure of merit based on the statistics of the values of $\alpha$. In Germain, Main & Woolfson (1970) it was shown that the expected value of $\alpha_{\mathbf{h}}^2$, $\langle\alpha_{\mathbf{h}}^2\rangle_e$, is given by

$$\langle\alpha_{\mathbf{h}}^2\rangle_e = \sum_{\mathbf{h}'} K_{\mathbf{h},\mathbf{h}'}{}^2 + 2\sum_{\mathbf{h}'}\sum_{\substack{\mathbf{h}''\\ \mathbf{h}'\neq\mathbf{h}''}} K_{\mathbf{h},\mathbf{h}'}K_{\mathbf{h},\mathbf{h}''}\,\frac{I_1(K_{\mathbf{h},\mathbf{h}'})}{I_0(K_{\mathbf{h},\mathbf{h}'})}\,\frac{I_1(K_{\mathbf{h},\mathbf{h}''})}{I_0(K_{\mathbf{h},\mathbf{h}''})}$$

where

$$K_{\mathbf{h},\mathbf{h}'} = 2\sigma_3\sigma_2{}^{-3/2}|E_{\mathbf{h}}E_{\mathbf{h}'}E_{\mathbf{h}-\mathbf{h}'}|\,.$$

For a random set of phases the expectation value of $\alpha_{\mathbf{h}}^2$ is given by

$$\langle\alpha_{\mathbf{h}}^2\rangle_r = \sum_{\mathbf{h}'} K_{\mathbf{h},\mathbf{h}'}^2\,. \tag{17}$$

One can thus use as an absolute figure of merit

$$M_{\text{abs}} = \frac{Z - \sum_{\mathbf{h}}\langle\alpha_{\mathbf{h}}^2\rangle_r^{1/2}}{\sum\langle\alpha_{\mathbf{h}}^2\rangle_e^{1/2} - \sum\langle\alpha_{\mathbf{h}}^2\rangle_r^{1/2}}\,. \tag{18}$$

Table 4. *Values of* $\alpha'_{\mathbf{h}}$

Computer output for *FASTAN* for a trial structure.

```
                    RAFFINOSE          FASTAN PHASE DETERMINATION                    11  JUNE  1970


STARTING PHASES INPUT FROM CARDS

FOURIER OUTPUT NOT REQUIRED




SET NO.    1              SIGMA ALPHA =  0.31337E+04            ABSOLUTE FIGURE OF MERIT =  1.1321

  H   K   L  PHI  ALPHA     H   K   L  PHI  ALPHA     H   K   L  PHI  ALPHA     H   K   L  PHI  ALPHA     H   K   L  PHI  ALPHA
  0   0   8    0   17.4     0   0  12  180   44.6     0   1   6   90   30.2     0   1  14   90   13.1     0   1  18  270    8.9
  0   1  20   90   12.8     0   1  25   90    7.9     0   2   4  180   50.6     0   5   3   90   11.1     0   5   9  270    5.1
  0   5  16  270   11.8     0   6   4  180    9.6     0   6   7    0   10.7     0   6  12  180   42.8     0   6  13  180   13.2
  0   6  14    0   17.0     0   6  19  180    7.7     0   7   8  270   14.7     0   7  12   90    6.5     0   7  14   90   16.8
  0   7  28   90   40.8     0   8   0    0   18.4     0   8   8    0    4.9     0   8  12  180   11.2     0   8  19  180    0.7
  0   9  16  270    0.6     0   9  21  270   18.9     0  10   3    0    7.2     0  11   6  270    8.1     0  11  11   90    3.4
  0  11  14  270    2.1     0  12   1    0   21.6     0  12  13  180    3.9     1   0   6    0   22.9     1   0   9   90   10.2
  1   0  15   90   16.7     1   0  16  180    2.5     1   1  11  299   19.8     1   2   9  166    5.3     1   2  13  211   12.7
  1   4  15  235   15.6     1   4  25  261    8.2     1   4  26  118    5.1     1   5   1  149   15.0     1   5   2   72   19.3
  1   6  17  128   12.3     1   6  25  150   24.2     1   7  14  280   25.2     1   7  15  263   26.0     1   7  19   33    6.1
  1   8  10  155   11.7     1   8  14  174   12.2     1   8  21  332   18.7     1   9   5  309    6.1     1  11   5  182   22.0
  1  10   6  270   11.6     1  11   7  338    4.0     1  11   8   86    6.4     1  10  10    4   42.0     2   0   3  270   45.9
  2   2  17  344    7.1     2   3   3  231    5.0     2   4   3   68    7.1     2   4  13  186    8.6     2   4  17   12    1.8
  2   4  20  257   21.1     2   5  17  182    6.7     2   5  20  220   14.0     2   5  24  354   16.9     2   6  16   73   22.5
  2   7   3  335    2.2     2   7   5  189   15.7     2   7  14   99    3.8     2   7  17   17   13.4     2   8  14   19    9.1
  2   9   3  226   36.1     2   9   5  306   14.8     2   9  12  112    3.9     2   9  13  318   15.3     2  10   1  301   46.6
  2  10   7  268   10.2     2  11   1  159   26.4     2  10   2  228    5.2     2  10   3   57   22.2     2  11   7   63    5.9
  2  10   8   38    7.8     2  10   9  304   13.9     2  11   9  176   10.7     2  11  16  328   14.1     2  11  17  173   21.9
  2  10  18  262    1.8     2  14   3  277    8.0     3   0  18    0   22.9     3   1  19  299   10.6     3   2  20  334   18.4
  3   3   7  166   18.0     3   3  19   13    9.9     3   3  23  149   12.1     3   4  13  268   12.1     3   6  16  262    5.8
  3   6  20   11    8.3     3   7   1   11   14.3     3   7  11  160   30.7     3   8  14  310    9.8     3   9   0  270    3.1
  3   9  19   19   14.6     3  10  12  159    2.9     3  11   1  180    8.1     3  11   3   34   13.0     3  10   5  260   56.9
  3  10   7  294   29.7     3  11  11    6   14.4     3  10  13  276   12.1     3  11  15  200    9.7     3  13   1   66    5.3

  4   0  17  270   23.2     4   0  20    0    3.0     4   1   0  180   18.4     4   1   5   71   27.7     4   1  16  106   28.5
  4   1  18   73   26.4     4   1  19  170    3.2     4   2  17  310   15.7     4   3  19  180   13.4     4   3  21  210    9.6
  4   4  21  126   23.3     4   5  17   96   15.6     4   7  13  335    7.5     4   7  16   94   23.6     4   8   4  344   37.0
  4   8   5  103    1.6     4   9   8  235   10.1     4  10   4  177   25.7     4  10  10  167    9.2     4  13   0    0    4.6
  5   0   6  180   16.7     5   0  14  180   33.8     5   0  17  270    5.9     5   1  10  312    5.9     5   1  14  117   18.6
  5   1  24   68   10.1     5   2   0   90   11.9     5   2  12  305    6.4     5   4   8  173   25.6     5   5  15   35   18.2
  5   5  20   31    6.9     5   6   2  320    5.8     5   7   0   90    7.8     5   7   2  338   40.6     5   7   3  174   10.6
  5   7   9   27   17.0     5   7  12  264   26.7     5   7  14  132   23.9     5   8   2    6    8.1     5   8   4  287   40.9
  5   8  16   57   15.3     5   9   5  243   16.0     5   9  10  333   20.0     5   9  11  192    2.1     5  10   6  318    6.7
  5  11   8  253   14.3     6   0  14  180    3.6     6   0  18  180    1.8     6   0  21  270   12.7     6   1  13  350   17.0
  6   1  19    6    4.9     6   2  16  281   11.2     6   3   1  317    7.4     6   3   9  234    2.9     6   3  13  178   30.3
  6   3  18  142    4.3     6   4   7   75   12.3     6   4  18  333    9.9     6   7   1  219   14.6     6   7  11  162    5.2
  6   7  13   10    9.6     6   7  16  295   13.8     6   8   3  250   17.7     6   8   8   94    6.5     6   9   4  163   13.6
  7   0   8    0    1.6     7   0  13   90    5.6     7   0  15   90    5.6     7   0  18    0    3.0     7   1   2  249   26.8

  7   1   7  262   13.5     7   2   1  235   48.8     7   2   9  245   42.8     7   3   1   13   13.6     7   3   3  138   34.5
  7   3  11  155   22.0     7   4   3  263   38.4     7   4   5   71   26.1     7   4  13   83   11.8     7   4  18  197    4.7
  7   7   0   90    9.7     7   7   5  270    3.5     7   8   2   67   11.8     7   8  11  315    7.5     7   9  10  115   11.2
  7   9  11  189   12.8     8   1   2  164   20.3     8   1  15  127   10.8     8   2   8  212   26.2     8   3   5  345    8.5
  8   3   9  159    7.8     8   3  17  168   27.0     8   4   3   97    5.8     8   4   4   23   16.4     8   4  16  200    6.6
  8   5   5   16    7.2     9   3  11  327    5.6    10   0   8  180    2.0

END
```

Table 5. *Computer output for the computer program CONVERGE*

The beginning and end of the program are shown.

```
                 CONVERGENCE WITH SIGMA ONE      RAFFINOSF                    11  JUNE  1970

NUMBER OF SETS OF PHASES PRODUCED IS LIMITED TO   32

MINIMUM ESTIMATED ALPHA IS   0.50

HIGH E'S ONLY USED FOR SIGMA 1

SIGMA 1  RESULTS

SIGN ACCEPTED IF PROBABILITY GREATER THAN  0.5700

          CODE    H    K    L     PROB           CODE    H    K    L     PROB           CODE    H    K    L     PROB
             1    0    0    8    0.7282             2    0    0   12    0.0717             8    0    2    4    0.4374
            12    0    6    4    0.5000            14    0    6   12    0.5000            16    0    6   14    0.6079
            22    0    8    0    0.5000            23    0    8    8    0.5951            24    0    8   12    0.5000
           117    4    0   20    0.5000           162    6    0   14    0.3774           163    6    0   18    0.5000
           213   10    0    8    0.7142


TOTAL ESTIMATED ALPHA IS  0.2903E+04

TOTAL  RANDOM  ALPHA  IS  0.1154E+04


CONVERGENCE MAPPING

   26       0   9  16      2.29     21   -8  0  1.67    165 -178  0  1.14
   25       0   8  19      2.65    140  157  1  1.29     40   56  0  1.23    141 -157  1  1.19
   31       0  11  14      2.90    121  133  0  1.42     94  110  1  1.41     90   60  1  1.14
  169       6   3   9      3.47     55 -155  0  1.61    165   -8  0  1.18     29 -178  1  1.17    -48  193  1  1.13
  195       7   4  18      3.49     89 -149  1  1.58     17  187  1  1.20     11 -165  1  1.18   -145   76  0  1.17
  181       7   0   8      3.81    157  -76  0  1.31      3 -185  1  1.19     89  161  0  1.19     18 -196  1  1.17
                                    79  157  0  1.12
  159       5   9  11      3.86     56 -119  0  1.35   -204 -109  0  1.26   -167   55  0  1.17     69  -99  0  1.13
                                   144    9  0  1.13
   30       0  11  11      3.86    200 -187  1  1.94     16   -9  1  1.19     43   49  0  1.19     34  -55  0  1.17
   43       1   4  26      3.82     47   80  0  1.55    -70  -59  1  1.52   -164  193  0  1.25     66  -34  1  1.17
  208       8   4   3      4.07     21  207  1  1.63   -207  -20  0  1.22     34 -192  0  1.14    125 -121  0  1.14
                                     6 -207  1  1.12
  166       6   1  19      4.08    -49  155  0  1.79     53  149  0  1.50    120   60  0  1.28    -46  149  1  1.19
  163       6   0  18      4.20     52 -155  0  1.43     75 -130  0  1.28    113 -110  1  1.25     49 -150  0  1.23
                                    41  192  0  1.21
  175       6   7  11      4.23      2 -174  1  1.61     47 -140  1  1.22   -204  -76  1  1.21     70 -119  1  1.21
                                   188  -45  0  1.18
  117       4   0  20      4.31    137  -34  1  1.50    121  202  0  1.44    203  119  1  1.23      7  119  1  1.21
                                     6 -118  1  1.16
   58       1  11   8      4.45     27  -40  0  1.83    -55   60  0  1.29   -129 -144  0  1.21    112   60  1  1.17
                                   177  144  0  1.15
  107       3  10  12      4.63    204 -155  1  1.72    137   83  0  1.47   -158  202  0  1.28     36  -84  1  1.27
                                   -38   82  0  1.14
   57       1  11   7      4.67      2  -55  0  1.81   -111  118  1  1.54   -123 -158  1  1.21   -144 -174  0  1.17
                                    95   79  0  1.17
  131       4   8   5      4.77     27  120  1  1.81    123  -14  0  1.55     47  -95  1  1.27    116  -24  0  1.24
                                   -35 -155  0  1.15



  153       5   7  14      4.68      2  149  0  2.46   -140   22  1  1.80    158   -8  0  1.55
  140       5   1  14      3.68    -14  149  0  2.53     24 -149  1  1.71
   24       0   8  12      3.99      2   22  0  2.47     47   40  1  1.41     53   35  1  1.21
   22       0   8   0      2.47     12   -8  0  1.79     23   -1  0  1.20
   47       1   6  25      4.48     66  110  0  2.35     53   -8  0  1.91     70  -35  1  1.35
   66       2   4  20      4.46    -14   86  0  1.93     70   -8  0  1.69     70  133  0  1.78
   70       2   6  16      2.29     95 -155  0  2.29
   86       2  10   8      3.58     93   59  0  1.96    116   87  1  1.40     53  -40  0  1.33
   93       3   0  19      4.02    123  187  1  2.43    126 -192  1  2.14
   53       1   8  21      4.23   -116  155  0  2.66    -95  -80  0  2.13
   95       3   2  20      3.47    123  192  1  2.08   -126  187  1  1.94
  123       4   2  17      3.62    126    8  0  1.72    -51  111  0  1.67   -126  -12  1  1.35
  126       4   4  21      1.69   -116  209  0  1.69
  116       4   0  17      4.07     59 -111  1  2.75    162  -60  0  1.87
  209       8   4   4      4.71     14  204  0  2.03    204   -8  0  1.66     40 -188  0  1.43   -204  -12  0  1.30
  204       8   2   8      3.87    133 -130  0  1.96     35 -187  0  1.55    -40 -193  1  1.49
   40       1   2  13      3.06   -162 -187  0  1.61     35    8  0  1.31     51   84  1  1.22
   51       1   8  10      4.64    137  130  0  2.13    162  155  0  1.58    158  118  0  1.34    136 -130  0  1.29
  158       5   9  10      4.17     59 -118  1  1.87      3  155  0  1.75   -188  -62  0  1.68
   14       0   6  12      4.74    188 -192  1  2.55     23   -8  0  1.82      1   12  0  1.50
   12       0   6   4      4.25    192 -187  1  1.84    193  187  1  1.54    188  193  1  1.37     23    8  0  1.17
  130       4   8   4      4.84   -110  187  0  2.85   -188  110  0  2.54
  188       7   2   9      4.73    193   -8  0  1.75      1  187  0  1.60     16  193  1  1.60     -3  190  1  1.50
  193       7   4   5      3.64      8  187  0  1.97      1 -192  0  1.43     23  192  1  1.36
    8       0   2   4      3.68    192  187  0  2.35     76   82  1  1.89
  192       7   4   3      3.32   -149   82  1  2.24      3 -190  0  1.64
   82       2  11   1      3.71   -155 -190  1  2.20    -60  118  0  2.06
  190       7   3   3      2.15   -149   80  1  2.15
  149       5   7   2      3.78    -76  187  0  2.21     -3 -155  0  2.13
  187       7   2   1      2.35   -155  -84  1  2.35
  155       5   8   4      0.01
   76       2   9   3      3.20    -84 -118  1  1.66     -3  -84  0  1.41     87    3  1  1.23
   84       2  10   3      1.88      2  -87  1  1.68
   87       2  10   9      3.22    137  110  1  2.48      1   80  0  1.28
  137       5   0  14       .54     59 -133  0  2.67      1  136  0  1.53    213 -136  1  1.47
  133       4  10   4      4.21     60   80  0  1.99     35 -110  0  1.74    -59 -136  0  1.61
  136       5   0   6      3.37    110  -80  1  2.06    111   80  0  1.87
   80       2  10   1      1.72     59  -35  0  1.72
   59       1  10  10      2.34    111  -60  0  2.34
  111       3  10   7      3.65      2 -110  0  3.65
  110       3  10   5      0.01

KNOWN PHASES
      CODE    H    K    L   PHI 100*WT         CODE    H    K    L   PHI 100*WT         CODE    H    K    L   PHI 100*WT
         1    0    0    8   360    46             2    0    0   12   180    86            16    0    6   14   360    22
        23    0    8    8   360    19           162    6    0   14   180    25           213   10    0    8   360    43

ORIGIN FIXING REFLEXIONS
    CODE    H    K    L   PHI      CODE    H    K    L   PHI      CODE    H    K    L   PHI      CODE    H    K    L   PHI
       3    0    1    6    90        35    1    0    9    90        60    2    0    3    90       118    4    1    0   360

OTHER REFLEXIONS IN STARTING SET
    CODE    H    K    L            CODE    H    K    L            CODE    H    K    L            CODE    H    K    L
     110    3   10    5             155    5    8    4

NUMBER OF SETS OF PHASES WRITTEN ON TAPE 74 IS   16

  END
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The value of $M_{\mathrm{abs}}$ would tend to be near zero for random phases and of order unity for correct phases. In practice correct sets of phases are found to give values of $M_{\mathrm{abs}}$ in the range about $1{\cdot}0-1{\cdot}4$. While some incorrect sets of phases can also give values of $M_{\mathrm{abs}}$ of this magnitude it is unlikely that correct phases would give $M_{\mathrm{abs}}$ as low as 0·7, say. It should be stressed that no theoretical relationship has been found between $M_{\mathrm{abs}}$ and the probability of a set of phases being correct and that quoted judgments of the significance of values of $M_{\mathrm{abs}}$ are based on present experience – as yet limited.

Table 4 shows the value of $M$ as 1·13 for the correct set of phases for raffinose (Berman, 1970) a trial structure for trying out methods.

Provision is made in *FASTAN* for the input of starting phases from cards. This is particularly useful when a recycling procedure is being used in which a number of phases have been calculated from a partial structure and are to be used as a basis for further phase determination. In this case it is advisable to fix most of the input phases for the initial stages of phase determination. This ensures that the new phases determined conform to the input information before refining all the phases together. If the input phases are allowed to refine immediately it is not uncommon for them to change their values completely so they bear no relation to those input.

We wish to express our gratitude to the North Atlantic Treaty Organization for supporting liaison between our laboratories and also to the Science Research Council for its continuing support of our activities in York. We also wish to give thanks to the referee whose constructive criticisms of the first version of this paper led to a number of improvements in the presentation of the material.

### References

Berman, H. M (1970). *Acta Cryst.* **B26**, 290.

Cochran, W. & Woolfson, M. M. (1955). *Acta Cryst.* **8**, 1.

Evrard, G. (1971). *Acta Cryst.* Submitted for publication.

Germain, G. & Woolfson, M. M. (1968). *Acta Cryst.* **B24**, 91.

Germain, G., Main, P. & Woolfson, M. M. (1970). *Acta Cryst.* **B26**, 274.

Hauptman, H. & Karle, J. (1953). *Solution of the Phase Problem.* I. *The Centrosymmetric Crystal.* A.C.A. Monograph No. 3.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849.

Klug, A. (1958). *Acta Cryst.* **11**, 515.

Woolfson, M. M. (1956). *Acta Cryst.* **9**, 804.

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*Acta Cryst.* (1971). A**27**, 376

# Short-Range Ordering of Vacancies and Fermi Surface of TiO

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The structure of the disordered (high-temperature) phase of titanium monoxide has been studied by electron diffraction. Composition-dependent complex distributions of diffuse scattering are observed and interpreted in terms of short-range-ordered configurations of lattice vacancies. The proposition that the form of the diffuse scattering may correspond to ordering under the influence of long-range electronic energy terms and so show a direct relationship to the topology of the Fermi surface is examined.

## Introduction

The titanium monoxide phase has statistically the NaCl type structure at high temperatures and is stable over a wide composition range *e.g.* from $TiO_{0\cdot70}$ to $TiO_{1\cdot25}$ at 1400°C and from $TiO_{0\cdot90}$ to $TiO_{1\cdot25}$ at 900°C and lower temperatures. The structure contains a large proportion of vacancies of both titanium and oxygen, the relative number of each type depending on composition. For $TiO_{1\cdot0}$ 15% of both kinds of site are vacant while $TiO_{1\cdot25}$ has all oxygen sites full but 22% of the titanium sites empty.

Below a certain composition-dependent critical temperature, varying from 990°C for $TiO_{1\cdot0}$ to about 750°C for $TiO_{1\cdot25}$, super-lattice structures are formed by the ordering of vacancies. These have been analysed by Watanabe, Castles, Jostsons & Malin (1967) and Watanabe, Terasaki, Jostsons & Castles (1968, 1969) on the basis of electron diffraction single-crystal patterns and by Hilti (1968) using X-ray diffraction patterns taken from crystals having a single orientation with respect to the basic NaCl-type structure but com-

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