Acta Cryst. (1983). A**39**, 98–101

Determination of a Centrosymmetric Crystal Structure using Experimentally Determined Phases with the Direct Method

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(*Received* 24 *February* 1982; *accepted* 12 *August* 1982)

Abstract

The relation $S_P = S_L S_R$ between the signs of the triplet phase products S_P, the multiple diffraction line profiles S_L and the crystal lattice rotations S_R is applied to the structure determination of a centrosymmetric $Cs_{10}Ga_6Se_{14}$ crystal [space group $C2/m$, a = 18·233 (7), b = 12·889 (5), c = 9·668 (3) Å, β = 108·2°, Z = 2]. This structure could not be solved by the ordinary *MULTAN* program, including *MULTAN*-80. From the profile analysis of the multiple diffraction pattern of $\bar{3}11$ using a four-circle single-crystal diffractometer with Cu $K\alpha$ radiation, 12 phase relations among closely linked reflections are determined. Four possible sets of 14 reflection phases are deduced. Using these four sets as the starting phases for *MULTAN*-74, 225 correct phases are developed. The final E map shows all the atomic positions of Cs, Ga and Se. The structure refinement gives R = 0·047, R_w = 0·053 [1907 reflections with $I > 2\sigma(I)$]. Details about the procedure are given.

Introduction

Attempts to determine X-ray diffraction phases experimentally have been made by many investigators, including Lipscomb (1949), Hart & Lang (1961), Post (1977) and Chapman, Yoder & Collella (1981). A recently proposed method (Chang, 1982) provides a proper means of determining the phases for a centrosymmetric structure. In this method, the sign, S_P, of a triplet phase product of the structure factors $F_{-\mathbf{H}_1}F_{\mathbf{H}_2}F_{\mathbf{H}_1-\mathbf{H}_2}$ can be obtained by the relation:

$$S_P = S_L S_R. \qquad (1)$$

$\mathbf{H}_1$, $\mathbf{H}_2$ and $\mathbf{H}_1 - \mathbf{H}_2$ are the primary, the secondary and the coupling reflections involved in a three-beam multiple Bragg reflection. S_L is the sign defined from the three-beam multiple diffraction line profile. S_R is the sign depending on whether the secondary reciprocal-lattice point is entering (incoming) or leaving (outgoing) the Ewald sphere during the crystal rotation around the reciprocal-lattice vector $\mathbf{H}_1$. The signs of S_L and S_R are given in Table 1. The practical use of this method, in conjunction with the direct method, has been given to determine the structure of diamond as a simple example (Chang & Han, 1982).

In this paper, we report the application of the experimentally determined phases to the rather difficult crystal structure of $Cs_{10}Ga_6Se_{14}$. This structure has recently been determined (Deiseroth & Han, 1981) using the Patterson method with great effort, after the failure of *MULTAN* (see Fig. 1). However, the structure is redetermined, with ease, using the experimentally determined phases together with the direct method.

Table 1. *Definition for S_L of line profiles and S_R of the crystal lattice rotation*

S_l	∧	+
	∨	−
S_r	INCOMING	+
	OUTGOING	−

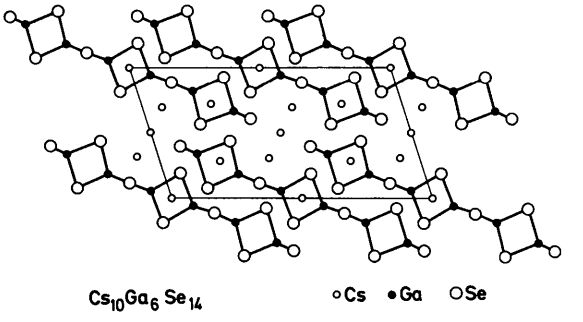

Fig. 1. Crystal structure of $Cs_{10}Ga_6Se_{14}$.

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0567-7394/83/010098-04$01.50

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Experiment

A $Cs_{10}Ga_6Se_{14}$ crystal of size 0·1 × 0·1 × 0·1 mm was mounted on a $P\bar{1}$ Syntex four-circle diffractometer. A fine-focus Cu tube and a graphite monochromator provided an incident beam with 6′ angular divergence. The ψ scan about the primary reflection was carried out at 0·05° min^{-1}. The intensity of the primary reflection is monitored by a scintillation counter and recorded on a rolling chart. The other experimental conditions were the same as those previously reported (Chang & Han, 1982). Normal data collection was carried out, using Mo $K\alpha$ radiation, in the usual way for crystal structure determination. The next step was to obtain three-beam multiple diffraction line profiles. The following procedure was followed:

(*a*) *Choice of the primary reflection* $\mathbf{H}_1$

In order to have optimal conditions for obtaining well defined and useful line profiles, the following facts should be considered.

(1) Weak reflections need to be used as the primary reflections so as to obtain better signal-to-noise ratios.

(2) There must be enough three-beam (except for some special cases discussed below) diffractions with strong secondary and coupling reflections. The reflections (two-beam) which lie on the bottom of the convergence map of *MULTAN* should be frequently involved in these three-beam cases.

(3) The triplet phase relations from the three-beam cases ought to link the involved reflections, either the secondary or the coupling reflections, to form a link diagram like Fig. 3 (Chang & Han, 1982).

(4) The χ angle of the primary reflection should be in such a range that the primary reflection is a Bragg case during the ψ scan around $\mathbf{H}_1$.

In practice, the data collection for $Cs_{10}Ga_6Se_{14}$ shows 1907 independent reflections for $\sin\theta/\lambda$ between 0 and 1·15 Å^{-1} ($0 < 2\theta \leq 55°$), namely, $0 \leq h \leq 19$, $0 \leq k \leq 14$ and $-10 \leq l \leq 10$. Among these, 82 reflections are strong with intensities greater than 1500 counts s^{-1} and 491 reflections are weak with intensities less than 300 counts s^{-1}. Treating these strong reflections as the secondary reflections $\mathbf{H}_2$ and as the coupling reflections $\mathbf{H}_3$, the corresponding primary reflection set is given by $(\mathbf{H}_2 + \mathbf{H}_3)$. These additions among the strong reflections generating 20 weak reflections, which appear frequently in the results of additions, are listed in Table 2. The corresponding frequencies are included.

The reflection $31\bar{1}$, according to Table 2, appears most frequently, which means that the number of useful three-beam reflections generated by using $31\bar{1}$ as the primary reflection is a maximum. (The same addition procedure using the last 30 reflections of the convergence map shows also that the $31\bar{1}$ is the most suitable primary reflection.) The $\bar{3}11$ is the best choice among $\{31\bar{1}\}$, since $\chi = 76·08°$ for the crystal at the Bragg condition for $\bar{3}11$.

Table 2. *The frequency for 20 weak reflections appearing in phase relations*

Index	Frequence	Index	Frequence
4 4 $\bar{3}$	20	0 2 $\bar{2}$	5
0 2 2	5	1 3 0	22
2 2 1	26	1 1 0	22
3 1 $\bar{2}$	18	3 1 2	12
3 1 $\bar{1}$	34	5 1 $\bar{3}$	24
1 3 3	10	2 2 3	19
2 2 0	13	4 4 $\bar{1}$	14
4 2 $\bar{1}$	13	4 4 3	8
5 3 2	17	4 0 2	7
0 0 1	22		

(*b*) *Choice of the wavelength and indexing the multiple diffraction pattern*

We know that long-wavelength radiation, which is suitable for resolving the overlapping of multiple diffraction peaks, can also provide clear line profiles for phase determination. For this purpose, Cu $K\alpha$ radiation is used to obtain a multiple diffraction pattern of $\bar{3}11$. The recently proposed method of indexing multiple diffraction peaks (Han & Chang, 1982) is used to identify each peak without ambiguity. Because of the twofold symmetry of the multiple diffraction pattern caused by the rotation around $\bar{3}11$, a ψ scan of more than 180° is, in principle, necessary.

Results

(*a*) *Multiple diffraction pattern and the phase relation*

The multiple diffraction pattern of $\bar{3}11$ for Cu $K\alpha$, ranging from $\psi = -100$ to 80°, is shown in part in Fig. 2. Not all the diffracted peaks were used. Only those having well defined profile asymmetry were

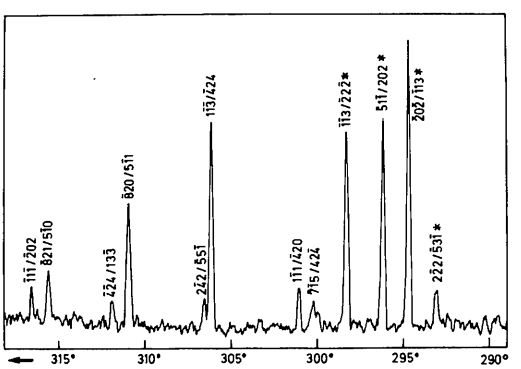

Fig. 2. $\bar{3}11$ multiple diffraction pattern of $Cs_{10}Ga_6Se_{14}$ for Cu $K\alpha$. Peaks marked with asterisk are used in the phase determination.

selected. For example, in Fig. 2, only those peaks marked with asterisks were considered. Table 3 gives the indices of the selected three-beam diffraction peaks, together with the indication of the relative rotation of the secondary reciprocal-lattice points with respect to the Ewald sphere. The signs of the triplet phase products are obtained experimentally from the products of S_L and S_R. As an example, the peak at $\psi = 295{\cdot}2°$ has a positive S_L, according to Table 1, and is in an incoming situation ($S_R = +1$). The sign of the triplet phase, S_P, is therefore positive. From these triplet phase relations and the symmetrically equivalent relations of $C2/m$ [$\varphi(hkl) = \varphi(\bar{h}\bar{k}\bar{l}) = \varphi(h\bar{k}l) = \varphi(\bar{h}k\bar{l})$], a diagram showing the linking between the involved reflections (both the secondary and the coupling reflections) can be constructed as shown in Fig. 3. From Fig. 3(*b*) eight nonequivalent equations of the type $S_1S_2S_3 = \pm 1$ can be derived which allow one to recognize phase relationships for the reflections:

$$S(11\bar{3}) = S(511) = -S(531) = -S(13\bar{3})$$
$$S(202) = -S(222) = -S(820) = -S(42\bar{4}) \qquad (2)$$
$$S(\bar{3}11)\,S(202)\,S(11\bar{3}) = +1.$$

The space group $C2/m$ requires two reflections, which belong to either *ooo*, *eeo* or *ooe*, *eeo* parity groups, for fixing the origin of the unit cell. One of them can be found in the above reflections (for example, the reflection $11\bar{3}$ belongs to *ooo* parity group). Then the relation set (2) leads to two solutions [namely $S(202) = \pm 1$].

In Fig. 3(*a*), the link among 111, 420, 131, $22\bar{2}$ and $24\bar{2}$ gives the following relationships:

$$S(111) = S(131)$$
$$S(420) = S(22\bar{2}) = -S(24\bar{2}) \qquad (3)$$
$$S(\bar{3}11)\,S(111)\,S(420) = +1.$$

The combination of (*a*) and (*b*) of Fig. 3 leads to four solution sets (Table 4). Unfortunately, we cannot use any one of these reflections together with $11\bar{3}$ for fixing the origin. We must, therefore, consider all of the four sets to find a reflection of the *eeo* parity group suitable for the determination of the origin.

More individual phases can be determined if more weak reflections are used as primary reflections to generate more three-beam diffraction line profiles. On the other hand, the available direct method, for example the *MULTAN* program, provides a clue to developing more individual phases without carrying out further experiments. The four sets, *A*, *B*, *C* and *D*, of Table 4 serve as the starting sets for *MULTAN*.

Table 3. *Useful triplet phase products obtained from the* $\bar{3}11$ *multiple diffraction pattern of* $Cs_{10}Ga_6Se_{14}$

ψ (°)	S_R In or out	Secondary reflection	Coupling reflection	S_L	S_LS_R
260·8	out(−)	$\bar{4}\,2\,4$	$1\,\bar{1}\,\bar{3}$	+	−
271·6	out(−)	$\bar{1}\,1\,3$	$\bar{2}\,0\,\bar{2}$	−	+
293·6	out(−)	$2\,\bar{2}\,2$	$\bar{5}\,3\,\bar{1}$	−	+
295·2	in(+)	$\bar{2}\,0\,\bar{2}$	$\bar{1}\,1\,3$	+	+
296·6	in(+)	$\bar{5}\,1\,\bar{1}$	$2\,0\,2$	+	+
298·6	out(−)	$\bar{1}\,\bar{1}\,3$	$\bar{2}\,2\,\bar{2}$	+	−
320·8	in(+)	$\bar{4}\,2\,0$	$1\,\bar{1}\,1$	+	+
323·5	in(+)	$\bar{2}\,2\,\bar{2}$	$\bar{1}\,\bar{1}\,3$	−	−
328·4	in(+)	$\bar{5}\,3\,\bar{1}$	$2\,\bar{2}\,2$	+	+
332·3	out(−)	$\bar{2}\,\bar{2}\,2$	$\bar{1}\,3\,\bar{1}$	−	+
349·0	in(+)	$1\,3\,\bar{3}$	$\bar{4}\,\bar{2}\,4$	+	+
32·7	out(−)	$\bar{1}\,\bar{3}\,\bar{1}$	$\bar{2}\,4\,2$	+	−
57·7	in(+)	$1\,3\,1$	$\bar{4}\,2\,0$	+	+
63·3	out(−)	$\bar{5}\,\bar{1}\,\bar{1}$	$2\,2\,2$	+	−
76·2	out(−)	$\bar{8}\,2\,0$	$5\,\bar{1}\,1$	+	−

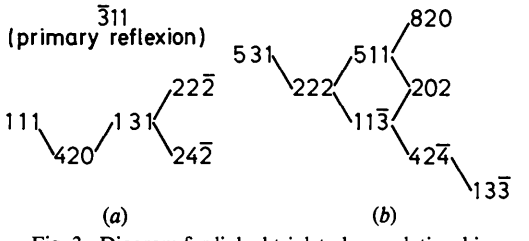

Fig. 3. Diagram for linked triplet phase relationships.

(*b*) *Combination of the experimental phases with the direct method*

Since the *MULTAN* program selects only those reflections whose E values are greater than the minimum E value, the reflections in the starting set, having small E, must be included manually. To stress that the phases associated with these reflections are correct, the weights of them are given to 0·99 in the tangent refinements. The additional reflection for fixing the origin is $4,10,\bar{7}$ decided by *MULTAN*.

The parameters and results of the *MULTAN* calculation are given in Table 5. Using sets *A*, *B*, *C* and *D* of Table 4 as the starting sets, columns *A*, *B*, *C* and *D* of Table 5 show the corresponding minimum E and

Table 4. *Possible starting phases for MULTAN*

Index	Phases of the solution sets *A*	*B*	*C*	*D*	*E*	Correct phase
$3\,1\,\bar{1}$	−	−	+	+	0·13	−
$1\,1\,1$	+	−	+	−	0·90	+
$1\,1\,\bar{3}$	−	−	−	−	2·39	−
$1\,3\,\bar{3}$	+	+	+	+	0·95	+
$1\,3\,1$	+	−	+	−	1·25	+
$2\,0\,2$	+	+	−	−	1·63	+
$2\,2\,2$	−	−	+	+	0·93	−
$2\,2\,\bar{2}$	−	+	+	−	2·24	−
$2\,4\,\bar{2}$	+	−	−	+	1·29	+
$4\,2\,\bar{4}$	−	−	+	+	2·75	−
$4\,2\,0$	−	+	+	−	1·55	−
$5\,1\,1$	−	−	−	−	2·45	−
$5\,3\,1$	+	+	+	+	1·13	+
$8\,2\,0$	−	−	+	+	2·31	−

Table 5. *MULTAN parameters and results*

Sets *A*, *B*, *C* and *D*: obtained using the known phases of set *A*, *B*, *C* and *D* in Table 4; set *E* and *F*: two sets of normal *MULTAN* results running without known phases.

	A	*B*	*C*	*D*	*E*	*F*
E_{min}	1·7	1·7	1·7	1·7	1·7	1·7
$E3_{min}$	2·7	2·7	2·7	2·7	2·7	2·5
Number of reflections used in *MULTAN*	225	225	225	225	205	296
Number of $\sum_2$ relations	3042	3042	3042	3042	2711	5836
Number of indeterminate phases	0	0	0	0	61	0
Percentage of correct phases in result (%)	100	60	59	50	61	75
ABS FOM	1·1343	1·1332	0·9906	0·9918	0·8080	1·0206
RESID	15·60	15·69	25·79	25·79	22·15	28·00

$E3$ values ($E3$ is the triplet product of E for $\sum_2$ relative reflections); the number of accepted reflections of the generated $\sum_2$ relations and of the indeterminate phases; the percentage of the correct phases; the absolute figure of merit (FOM); and the residual values. Columns *E* and *F* are the corresponding values determined from normal *MULTAN* calculation without using known phases. In comparison to the work of Deiseroth & Han (1981), the positions of the involved atoms obtained in this present work are correctly determined.

Discussion and conclusion

In practice, not only three-beam diffraction can be used for phase determination. When some of the involved secondary and coupling reflections in an *n*-beam case with $n > 3$ have relatively weak reflected intensities so that only a three-beam interaction dominates the whole diffraction process, this *n*-beam diffraction can be treated as a three-beam case. Under such a condition, this *n*-beam case can still be used as a three-beam case for phase determination.

We know that the use of a large starting set of many known phases can solve complicated structures using the normal direct method, for instance structures containing heavy atoms. The procedure described above provides a direct way of obtaining enough known phases to form a large starting set for *MULTAN*. The combination of the experimental phases with the direct method gives a new way of solving those difficult structures.

The authors are indebted to Professor H. Schenk for encouragement and useful discussions. The critical readings of this manuscript by Drs W. Nesper, H. J. Deiseroth and A. Arthur are also gratefully acknowledged.

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