

A Procedure for Identifying Enantiomorph-Defining Phases

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(Received 15 March 1982; accepted 15 July 1982)

Abstract

A computationally-convenient approach to identifying reflections which satisfy the formal conditions for enantiomorph definition is described.

1. Introduction

All application procedures in direct methods, when applied to noncentrosymmetric structures, require that one or more reflections are selected, in addition to those defining the cell origin, to specify the enantiomorph of the structure. The formal conditions that are required to specify the origin and the enantiomorph have been described in terms of the seminvariant vectors \mathbf{V} and seminvariant moduli \mathbf{m} by Hauptman & Karle (1956). The values of \mathbf{V} and \mathbf{m} are listed in § 6.1 of *International Tables for X-ray Crystallography* (1974).

General procedures for applying \mathbf{V} and \mathbf{m} in the selection of origin-defining reflections are well understood and widely applied in direct-methods computer software. In contrast, procedures for identifying enantiomorph-defining reflections (EDR) tend to be much less straightforward. As a result a significant number of errors and misconceptions about the general requirements for enantiomorphic definition continue to appear in publications, and even texts. This paper outlines a relatively simple and space-group-independent approach to enantiomorph definition suitable for both manual and computer-based application.

2. Enantiomorph definition

The origin of a cell is fixed by specifying the structure-factor phases of p linearly independent reflections (Hauptman & Karle, 1954, 1956). The value of p ranges from 0 to 3, and is determined by the space-group symmetry (Karle & Hauptman, 1956).

Any reciprocal-lattice vector \mathbf{h} can be expressed as a combination of the origin defining vector set $\mathbf{H} = (\mathbf{h}_1, \dots, \mathbf{h}_p)$ in the form

$$\mathbf{h} = \sum_j^p n_j \mathbf{h}_j \quad (1)$$

$$\mathbf{h} = \mathbf{nH}, \quad (2)$$

where \mathbf{n} is the vector set n_j ($j = 1$ to p). If all of n_j are integers then \mathbf{h} is *linearly* dependent on \mathbf{H} ; otherwise \mathbf{h} is *rationally* dependent on \mathbf{H} . The values of n_j ($j = 1$ to p) are determined from

$$\mathbf{n} = \mathbf{hH}^{-1}. \quad (3)$$

A detailed discussion on the linear and rational dependence of \mathbf{h} on \mathbf{H} is given by Rodgers (1980).

For the purposes of origin definition, a reflection vector \mathbf{h} is transformed into the seminvariant vectors \mathbf{h}' and \mathbf{u} by the operations

$$\mathbf{h}' = \mathbf{Vh} \quad (4)$$

and

$$\mathbf{u} = \mathbf{h}'(\text{mod } \mathbf{m}). \quad (5)$$

\mathbf{V} is the seminvariant vector matrix and \mathbf{m} are the seminvariant moduli (Hauptman & Karle, 1956). A necessary requirement of any set of origin-defining reflections is that the matrix of their seminvariant indices

$$\mathbf{U} = (\mathbf{u}_1, \dots, \mathbf{u}_p) \quad (6)$$

has the magnitude

$$|\mathbf{U}| = \pm 1. \quad (7)$$

Because of (7) any reflection \mathbf{h} , expressed as the seminvariant vector \mathbf{u} , is *linearly* related to \mathbf{U} by a set of integers n' (n'_1, \dots, n'_p) such that

$$\mathbf{n}' = \mathbf{uU}^{-1}. \quad (8)$$

If Φ is the set of origin defining phases (ϕ_1, \dots, ϕ_p) for the reflections $(\mathbf{h}_1, \dots, \mathbf{h}_p)$ then the linear relationship of \mathbf{u} to \mathbf{U} gives rise to a seminvariant phase ϕ'_h , where

$$\phi'_h = \mathbf{n}' \cdot \Phi. \quad (9)$$

For noncentrosymmetric structures the value of ϕ'_h provides an important means of identifying additional phases which are sensitive to the enantiomorphous structure. If the phase of an additional vector \mathbf{h} is equal to the value of ϕ'_h (modulus π) then ϕ_h is independent of the enantiomorph. On the other hand, if ϕ_h is significantly different (modulus π) to ϕ'_h then its application will, in principle, specify one of the enantiomorphs. In practice, enantiomorph specification is also dependent on vector \mathbf{h} forming strong

seminvariant relationships with the vectors $\mathbf{h}_1, \dots, \mathbf{h}_p$, and its ability to propagate \mathbf{h} on \mathbf{H} will, of course, be important to this latter requirement and is described in detail by Rodgers (1980). The general problem of choosing the optimal enantiomorph-defining reflection in terms of its connectivity will not be discussed here. This aspect of direct-phasing methodology is already adequately covered in the literature.

The purpose of this paper is to describe a procedure for applying the seminvariant phase φ_h in the identification of enantiomorph-defining reflections. The approach is applicable to all noncentrosymmetric space groups, except for the 22 space groups which form enantiomorphically-related pairs.

Three space groups $P2_12_12_1$, $P2_1$ and $P6_122$ have been selected to illustrate the application of this procedure. Two different sets of origin-defining reflections have been selected in each case and a variety of reflection classes are tested for enantiomorph discrimination. This procedure is embodied in the direct-methods software of the *XTAL* system (*GENTAN*; Hall, 1982).

3. Applications of the procedure

3.1. Space group $P2_12_12_1$ (type 1P222) (see Table 1)

For this space group the seminvariant vectors and moduli (see Table 6.1c, *International Tables for X-ray Crystallography*, 1974) are

$$\mathbf{v} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ and } \mathbf{m} = (2,2,2).$$

Example 1(a)

For the origin-defining reflections (ODR) $uu0$, $u0u$ and $u0g$ where

$$\varphi_{uu0} = \pi/2, \quad \varphi_{u0u} = \pi/2 \quad \text{and} \quad \varphi_{u0g} = 0,$$

$$\mathbf{U} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}; \quad |\mathbf{U}| = +1;$$

$$\mathbf{U}^{-1} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & -1 \\ 0 & 1 & -1 \end{pmatrix} \text{ and } \Phi = (\pi/2, \pi/2, 0).$$

(i) *Test uu0* (class 1, Table 1):

$$\mathbf{n}' = (1,1,0) \mathbf{U}^{-1} = (1,0,0)$$

and

$$\varphi' = (1,0,0) \Phi = \pi/2 \pmod{\pi}.$$

Since φ_{uu0} is restricted to $\pm\pi/2$, $uu0$ will not specify the enantiomorph.

(ii) *Test 0uu* (class 3, Table 1):

$$\mathbf{n}' = (0,1,1) \mathbf{U}^{-1} = (1, 1, -2)$$

and

$$\varphi' = (1, 1, -2) \Phi = 0 \pmod{\pi}.$$

Since φ_{0uu} is restricted to $\pm\pi/2$, $0uu$ will specify the enantiomorph.

(iii) *Test g0g* (class 11, Table 1):

$$\mathbf{n}' = (0,0,0) \mathbf{U}^{-1} = (0,0,0)$$

and

$$\varphi' = (0,0,0) \Phi = 0 \pmod{\pi}.$$

Since $\varphi_{g0g} = 0$ the reflection $g0g$ will not specify the enantiomorph.

(iv) *Test uuu* (class 13, Table 1):

$$\mathbf{n}' = (1,1,1) \mathbf{U}^{-1} = (1, 1, -1)$$

and

$$\varphi' = (1, 1, -1) \Phi = 0 \pmod{\pi}.$$

Table 1. Examples of enantiomorph definition reflections (EDR) in space group $P2_12_12_1$ (type 1P222) for two choices of origin

The flags * and + indicate that the enantiomorph would be specified if φ_h is significantly different from $(0,\pi)$ and $\pm\pi/2$, respectively. NR indicates that φ_h is not restricted in value.

Class	\mathbf{h}	\mathbf{u}	φ_h	φ'_h	EDR	Example (a)	Example (b)
						ODR = 1, 2, 7	ODR = 4, 5, 6
1	<i>uu0</i>	110	$\pm\pi/2$	$\pi/2$	no	$\pi/2$	no
2	<i>u0u</i>	101	$\pm\pi/2$	$\pi/2$	no	0	yes
3	<i>0uu</i>	011	$\pm\pi/2$	0	yes	$\pi/2$	no
4	<i>gu0</i>	010	$0, \pi$	$\pi/2$	yes	0	no
5	<i>ug0</i>	100	$\pm\pi/2$	0	yes	$\pi/2$	no
6	<i>g0u</i>	001	$\pm\pi/2$	$\pi/2$	no	$\pi/2$	no
7	<i>u0g</i>	100	$0, \pi$	0	no	$\pi/2$	yes
8	<i>0gu</i>	001	$0, \pi$	$\pi/2$	yes	$\pi/2$	yes
9	<i>0ug</i>	010	$\pm\pi/2$	$\pi/2$	no	0	yes
10	<i>gg0</i>	000	$0, \pi$	0	no	0	no
11	<i>g0g</i>	000	$0, \pi$	0	no	0	no
12	<i>0gg</i>	000	$0, \pi$	0	no	0	no
13	<i>uuu</i>	111	NR	0	*	0	*
14	<i>uug</i>	110	NR	$\pi/2$	+	$\pi/2$	+
15	<i>ugu</i>	101	NR	$\pi/2$	+	0	*
16	<i>guu</i>	011	NR	0	*	$\pi/2$	+
17	<i>ggg</i>	000	NR	0	*	0	*
18	<i>ggu</i>	001	NR	$\pi/2$	+	$\pi/2$	+
19	<i>gug</i>	010	NR	$\pi/2$	+	0	*
20	<i>ugg</i>	100	NR	0	*	$\pi/2$	+

$$\mathbf{U}^{-1} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & -1 \\ 0 & 1 & -1 \end{pmatrix} \quad \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Phi = (\pi/2, \pi/2, 0) \quad (0, \pi/2, \pi/2)$$

The unrestricted phase φ_{uuu} may be used to specify the enantiomorph provided its value is significantly different from 0 and π . For example, in a multiresolution process it could be applied with values between $\pi/4$ and $3\pi/4$.

Example 1(b)

For the origin-defining reflections $gu0$, $ug0$ and $g0u$, with $\varphi_{gu0} = 0$, $\varphi_{ug0} = \pi/2$, and $\varphi_{g0u} = \pi/2$,

$$\mathbf{U} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad |\mathbf{U}| = -1;$$

$$\mathbf{U}^{-1} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{and} \quad \Phi = (0, \pi/2, \pi/2).$$

(i) Test $u0u$ (class 2, Table 1):

$$\mathbf{n}' = (1,0,0) \quad \mathbf{U}^{-1} = (0,1,1)$$

and

$$\varphi' = (0,1,1), \quad \Phi = 0 \pmod{\pi}.$$

Since φ_{u0u} is restricted to $\pm\pi/2$, $u0u$ will specify the enantiomorph.

(ii) Test $0uu$ (class 3, Table 1):

$$\mathbf{n}' = (0,1,1) \quad \mathbf{U}^{-1} = (1,0,1)$$

and

$$\varphi' = (1,0,1) \quad \Phi = \pi/2 \pmod{\pi}.$$

Table 2. Examples of enantiomorph definition reflections (EDR) in space group $P6_122$ (type $3P_12$) for two choices of origin

The flags * and + indicate that the enantiomorph would be specified if φ_h is significantly different from $(0, \pi)$ and $\pm\pi/2$, respectively.

Class	h	u	φ_h	Example (a)		Example (b)	
				φ'_h	EDR	φ'_h	EDR
1	$0ku$	1	$0, \pi$	0	no	$\pi/2$	yes
2	$0kg$	0	$0, \pi$	0	no	0	no
3	$h0u$	1	$0, \pi$	0	no	$\pi/2$	yes
4	$h0g$	0	$0, \pi$	0	no	0	no
5	$hk0$	0	$0, \pi$	0	no	0	no
6	$hh1$	1	$5\pi/6, 11\pi/6$	0	yes	$\pi/2$	yes
7	$hh2$	0	$2\pi/3, 5\pi/3$	0	yes	0	yes
8	$hh3$	1	$\pm\pi/2$	0	yes	$\pi/2$	no
9	$hh4$	0	$\pi/3, 4\pi/3$	0	yes	0	yes
10	uuu	1	NR	0	*	$\pi/2$	+
11	uug	0	NR	0	*	0	*
12	ugu	1	NR	0	*	$\pi/2$	+
13	ugg	0	NR	0	*	0	*
14	ggu	1	NR	0	*	$\pi/2$	+

$$\mathbf{U}^{-1} = \begin{matrix} 1 & & \\ & 1 & \\ & & 1 \end{matrix} \quad \Phi = \begin{matrix} & & \\ & & \\ & & \end{matrix}$$

Since φ_{0uu} is restricted to $\pm\pi/2$, $0uu$ will not specify the enantiomorph.

3.2. Space group $P6_122$ (type $3P_12$) (see Table 2)

For this space group the seminvariant vectors and moduli (see Table 6.1c, *International Tables for X-ray Crystallography*, 1974) are

$$\mathbf{V} = (0,0,1) \quad \text{and} \quad \mathbf{m} = (2).$$

Example 2(a)

If the reflection class $0ku$ (designated class 1 in Table 2) is selected to specify the origin with φ_{0ku} set to 0, then

$$\mathbf{U} = 1; \quad |\mathbf{U}| = 1; \quad \mathbf{U}^{-1} = 1$$

and

$$\Phi = 0.$$

(i) Test $0ku$ (class 1, Table 2):

$$\mathbf{n}' = 1 \times \mathbf{U}^{-1} = 1 \quad \text{and} \quad \varphi' = 1 \times 0 = 0.$$

Since φ_{0ku} is restricted to 0 or π , $0ku$ will not specify the enantiomorph.

(ii) Test $0kg$ (class 2, Table 2):

$$\mathbf{n}' = 0 \times \mathbf{U}^{-1} = 0 \quad \text{and} \quad \varphi' = 0 \times 0 = 0.$$

Since φ_{0kg} is restricted to 0 or π , $0kg$ will not specify the enantiomorph.

(iii) Test $hh3$ (class 8, Table 2):

$$\mathbf{n}' - 1 \times \mathbf{U}^{-1} = 1 \quad \text{and} \quad \varphi' = 1 \times 0 = 0.$$

Since φ_{hh3} is restricted to $\pm\pi/2$, $hh3$ will specify the enantiomorph.

Example 2(b)

If the reflection class $hh3$ (designated class 8 in Table 2) is selected to specify the origin with a φ_{hh3} value of $\pi/2$, then

$$\mathbf{U} = 1; \quad |\mathbf{U}| = 1; \quad \mathbf{U}^{-1} = 1$$

and

$$\Phi = \pi/2.$$

(i) Test $0ku$ (class 1, Table 2):

$$\mathbf{n}' = 1 \times \mathbf{U}^{-1} = 1 \quad \text{and} \quad \varphi' = 1 \times \pi/2 = \pi/2.$$

Since φ_{0ku} is restricted to 0 or π , $0ku$ will specify the enantiomorph.

(iii) Test uug (class 11, Table 2):

$$\mathbf{n}' = 0 \times \mathbf{U}^{-1} = 0 \quad \text{and} \quad \varphi' = 0 \times \pi/2 = 0.$$

Since φ_{uug} is unrestricted, it may be used to specify the enantiomorph provided it has a value significantly different from 0 and π .

3.3. Space group $P2_1$ (1P202) (see Table 3)

For this space group the seminvariant vectors and moduli are

$$\mathbf{V} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ and } \mathbf{m} = (2,0,2).$$

Example 3(a)

Select the reflections $u0u$, $g0u$ and $01g$ to define the origin (reflection classes 2, 6 and 9 in Table 3). The phases φ_{u0u} and φ_{g0u} are restricted to 0 or π and are set at a value of 0. φ_{01g} is unrestricted but may be set at any value 0 to 2π . This is because the position of the origin in the y direction is arbitrary (*i.e.* $P2_1$ is a polar space group). It is important to emphasize that setting φ_{01g} to a non-zero (or non- π) value will *not* provide enantiomorphic discrimination. An additional phase φ_h with a value significantly different from φ' must be specified for this purpose. This also applies to space group $P1$, where three unrestricted phases are used to specify the origin.

Table 3. Examples of enantiomorph definition reflections (EDR) in space group $P2_1$, b unique (type 1P020), for two choices of origin

The flags * and + indicate that the enantiomorph would be specified if φ_h is significantly different from $(0, \pi)$ and $(q, \pi + q)$, respectively. In example (b) the value of q is assumed to be non-zero, non- π .

Class	h	u	φ_h	φ'_h	Example (a)	Example (b)	EDR	φ'_h	EDR
					ODR = 2, 6, 9	ODR = 3, 6, 15			
1	$uu0$	$1u0$	NR	0	*	q	+		
2	$u0u$	101	$0, \pi$	0	no	q	yes		
3	$0uu$	$0u1$	NR	0	*	0	*		
4	$gu0$	$0u0$	NR	0	*	0	*		
5	$ug0$	$1g0$	NR	0	*	q	+		
6	$g0u$	001	$0, \pi$	0	no	0	no		
7	$u0g$	100	$0, \pi$	0	no	q	yes		
8	$0gu$	$0g1$	NR	0	*	0	*		
9	$0ug$	$0u0$	NR	0	*	0	*		
10	$gg0$	$0g0$	NR	0	*	0	*		
11	$g0g$	000	$0, \pi$	0	no	0	no		
12	$0gg$	$0g0$	NR	0	*	0	*		
13	uuu	$1u1$	NR	0	*	q	+		
14	uug	$1u0$	NR	0	*	q	+		
15	ugu	$1g1$	NR	0	*	q	+		
16	guu	$0u1$	NR	0	*	0	*		
17	ggg	$0g0$	NR	0	*	0	*		
18	ggu	$0g1$	NR	0	*	0	*		
19	gug	$0u0$	NR	0	*	0	*		
20	ugg	$1g0$	NR	0	*	q	+		

$$\mathbf{U}^{-1} = \begin{pmatrix} 1 & -1 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad \Phi = (0,0,0)$$

$$\begin{pmatrix} 0 & -1 & 1 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \end{pmatrix} \quad (0,0,q)$$

For this example

$$\mathbf{U} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \quad |\mathbf{U}| = -1;$$

$$\mathbf{U}^{-1} = \begin{pmatrix} 1 & -1 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \text{ and } \Phi = (0,0,0).$$

(i) Test $uu0$ (class 1, Table 3):

$$\mathbf{n}' = (1, u, 0) \mathbf{U}^{-1} = (1, -1, u)$$

and

$$\varphi' = (1, -1, u) \Phi = 0.$$

Since φ_{uu0} is unrestricted, it may be used to specify the enantiomorph provided that its value is significantly different from 0 and π .

(ii) Test $u0g$ (class 7, Table 3):

$$\mathbf{n}' = (1, 0, 0) \mathbf{U}^{-1} = (1, -1, 0)$$

and

$$\varphi' = (1, -1, 0) \Phi = 0.$$

Since φ_{u0g} is restricted to 0 or π , it will *not* specify the enantiomorph.

Example 3(b)

Select reflection classes $01u$, $g0u$ and ugu to specify the origin, with $\varphi_{01u} = 0$, $\varphi_{g0u} = 0$ and $\varphi_{ugu} = q$. Then

$$\mathbf{U} = \begin{pmatrix} 0 & 1 & 1 \\ 0 & 0 & 1 \\ 1 & 0 & 1 \end{pmatrix}; \quad |\mathbf{U}| = 1;$$

$$\mathbf{U}^{-1} = \begin{pmatrix} 0 & -1 & 1 \\ 1 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \text{ and } \Phi = (0,0,q).$$

This example serves to illustrate a problem that occasionally occurs in direct methods. Whenever possible restricted phases are used to fix a cell origin. This is desirable so that the origin of the cell will be placed at points in the lattice which require these phases to be restricted. When existing restricted phases cannot be used for this purpose, either because of low $|E|$ values or insufficient reliable structure-invariant relationships with other reflections, it is necessary to use unrestricted phases to specify the origin. This situation is not to be confused with the use of unrestricted phases to specify the origin along polar axes through the arbitrary assignment of one (as in $P2_1$) to three (as in $P1$) unrestricted phases.

The use of the reflection ugu illustrates this difference. The unrestricted phase φ_{01u} may be set to some arbitrary value since it serves only to fix the origin on a polar y axis, but the phase φ_{ugu} (or for that matter any other unrestricted phase) must be assigned a value which conforms with the four permissible origins along (x,z) [i.e. $(0,0)$, $(\frac{1}{2},0)$, $(0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2})$], and the origin on the y axis fixed by $01u$.

The problem is that the value of φ_{ugu} is unknown at the start of a direct-methods process, and it is necessary to try a series of values between 0 and 2π . Typically, φ_{ugu} could be initiated at $\pi/4$, $3\pi/4$, $5\pi/4$, and $7\pi/4$ in four separate calculations and be permitted to vary in the final cycles of phase refinement. An interesting aspect of this procedure is that if the actual value of φ_{ugu} is significantly different from 0 and π , it will also serve to specify the enantiomorph, and the multi-solution process need only vary its value between 0 and π . However, if the value of φ_{ugu} happens to be close to 0 or π then another reflection must be specified to fix the enantiomorph. For this reason it is strongly recommended that an additional phase is specified for independent enantiomorphic discrimination.

(i) *Test uuu* (class 13, Table 3):

$$\mathbf{n}' = (1,u,1) \mathbf{U}^{-1} = (u,u,1)$$

and

$$\varphi' = (u,u,1) (0,0,q) = q.$$

Acta Cryst. (1983). A **39**, 26–28

The Probability of Large Structure Amplitudes: The Space Group $P\bar{1}$

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(Received 14 May 1982; accepted 6 August 1982)

Abstract

Application of limit theorems valid for large values of the sum of independent random variables shows that for an equiatomic structure with n atoms in the asymmetric unit in the space group $P\bar{1}$ the probability density distribution of the structure amplitude F for $|F|$ large is

$$p(x) dx = [n/2\pi(1-x^2)]^{1/2} (e/\pi)^{n/2} (1-x)^{(n-1)/2} dx$$

where $x = F/2nf$ is the unitary structure amplitude and

Since φ_{uuu} is unrestricted it may be used to specify the enantiomorph provided it is significantly different from q and $q + \pi$.

(ii) *Test 0uu* (class 3, Table 3):

$$\mathbf{n}' = (0,u,1) \mathbf{U}^{-1} = (u,g,0)$$

and

$$\varphi' = (u,g,0) (0,0,q) = 0.$$

Since φ_{0uu} is unrestricted, it may be used to specify the enantiomorph provided it has a value significantly different from 0 and π .

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f is the atomic scattering factor. The expression will be somewhat different for other space groups.

1. Introduction

The probability distribution of structure amplitudes is a special case of the random-walk problem. Expressions valid for resultants small compared with the maximum possible are readily available, but the standard sources do not give expressions valid for large resultants (Wilson, 1980). The present paper uses a limit theorem other than the central-limit theorem to derive an approximate distribution for large structure amplitudes in the space group $P\bar{1}$.

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