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A Unified Program for Phase Determination, Type $3P_2$

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The unified program for phase determination, valid for all the space groups and both the equal and unequal atom cases, is continued here. The present paper is concerned with the centrosymmetric space groups comprising type $3P_2$. A detailed procedure for phase determination is described for this type.

1. Introduction

This is the fifth in a series of papers concerned with a unified program of phase determination, initiated by us (Karle & Hauptman, 1959, hereafter referred to as $1P$). The application of the new probability methods, based on the Miller indices as random variables, is made here to the space groups of type $3P_2$ (Hauptman & Karle, 1953, 1959). This type consists of the three primitive centrosymmetric space groups of the rhombohedral system, the seven primitive centrosymmetric space groups of the cubic system, the two conventionally F-centered centrosymmetric space groups of the orthorhombic system and the six conventionally F-centered centrosymmetric space groups of the cubic system. The F-centered space groups are referred, in this paper, to the primitive unit cells defined in our paper on the seminvariants (Hauptman & Karle, 1959). Also listed in the latter paper is a set of coordinates for each space group. This is equivalent to choosing the functional form for the structure factor which is to be employed in the present paper. A detailed procedure for phase determination in the space groups of type $3P_2$ will be presented which utilizes the same general formula, and, at the same time, makes use of relationships among the structure factors characteristic of each space group.

2. Notation

The same notation as appears in $1P$ (1959) is employed here.

3. Phase determining formulas

3·1. *Basic formulas*

$$B_{2,0}\colon\ \mathscr{E}'^{2}_{\mathbf{h}}=1+\frac{4\pi\sigma_2^2}{2^{(p+q+2)/2}pq\Gamma\left(\frac{p+1}{2}\right)\Gamma\left(\frac{q+1}{2}\right)\sigma_4}\times\langle\lambda_{p\mathbf{k}}\lambda_{q(\mathbf{h}+\mathbf{k})}\rangle_{\mathbf{k}}+R_{2,0}\,. \quad (3\cdot1\cdot1)$$

$$B_{3,0}\colon\ \mathscr{E}'_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}_2}\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}=\frac{(2\pi)^{3/2}\sigma_2^3}{2^{(p+q+r+3)/2}pqr\Gamma\left(\frac{p+1}{2}\right)\Gamma\left(\frac{q+1}{2}\right)\Gamma\left(\frac{r+1}{2}\right)\sigma_4^{3/2}}\times\langle\lambda_{p\mathbf{k}}\lambda_{q(\mathbf{h}_1+\mathbf{k})}\lambda_{r(\mathbf{h}_1+\mathbf{h}_2+\mathbf{k})}\rangle_{\mathbf{k}}$$
$$-2\frac{\sigma_6}{\sigma_4^{3/2}}+\frac{\sigma_8^{1/2}}{\sigma_4}(\mathscr{E}'_{\mathbf{h}_1}\mathscr{E}'''_{\mathbf{h}_1}+\mathscr{E}'_{\mathbf{h}_2}\mathscr{E}'''_{\mathbf{h}_2}+\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}\mathscr{E}'''_{\mathbf{h}_1+\mathbf{h}_2})+R_{3,0}\,. \quad (3\cdot1\cdot2)$$

3·2. *Integrated formulas*

$$I_{2,0}\colon\ \mathscr{E}'^{2}_{\mathbf{h}}=1+\frac{2\sigma_2^2}{C_1^2(t)\sigma_4}\langle\Lambda_{t\mathbf{k}}\Lambda_{t(\mathbf{h}+\mathbf{k})}\rangle_{\mathbf{k}}+R'_{2,0}\,. \quad (3\cdot2\cdot1)$$

$$I_{3,0}\colon\ \mathscr{E}'_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}_2}\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}=\frac{\sigma_2^3}{C_1^3(t)\sigma_4^{3/2}}\langle\Lambda_{t\mathbf{k}}\Lambda_{t(\mathbf{h}_1+\mathbf{k})}\Lambda_{t(\mathbf{h}_1+\mathbf{h}_2+\mathbf{k})}\rangle_{\mathbf{k}}$$
$$-2\frac{\sigma_6}{\sigma_4^{3/2}}+\frac{\sigma_8^{1/2}}{\sigma_4}(\mathscr{E}'_{\mathbf{h}_1}\mathscr{E}'''_{\mathbf{h}_1}+\mathscr{E}'_{\mathbf{h}_2}\mathscr{E}'''_{\mathbf{h}_2}+\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}\mathscr{E}'''_{\mathbf{h}_1+\mathbf{h}_2})+R'_{3,0}\,. \quad (3\cdot2\cdot2)$$

In these formulas, p, q, r and t are restricted to be positive. Ordinarily they are given values in the range 2–4.

The remainder terms are given in the appendix, § 6 and in $1P$ (1959). Equation (3·1·1) or (3·2·1) serves to determine the magnitudes of the structure factors $|\mathscr{E}'_{\mathbf{h}}|$ corresponding to the squared structure. By means of equation (3·1·2) or (3·2·2), the phases of these structure factors $\varphi'_{\mathbf{h}}$ may be determined. In the next section we describe in detail how these equations are to be used.

4. Phase determining procedure

It is assumed that the $|\mathscr{E}_{\mathbf{h}}|$ have been calculated from the observed intensities. From these, the $|\mathscr{E}'_{\mathbf{h}}|$ are obtained by applying (3·1·1) or (3·2·1). In fact the $|\mathscr{E}'_{\mathbf{h}}|$, so computed, may be made to cover a range of reflections extending beyond that of the original set of observations. We are here concerned only with the

larger $|\mathscr{E}'_{\mathbf{h}}|$, and it is the phases of these whose values are to be determined. In the application of (3·1·2) or (3·2·2), the values of some $|\mathscr{E}'''_{\mathbf{h}}|$ may be required. These may be estimated from the corresponding $|\mathscr{E}_{\mathbf{h}}|$ or $|\mathscr{E}'_{\mathbf{h}}|$ or calculated from (3·1·1) or (3·2·1) in which $\mathscr{E}$ is replaced by $\mathscr{E}'$ and $\mathscr{E}'$ by $\mathscr{E}'''$, given sufficient data.

In the phase determining procedures to be described, it will be seen that the first steps concern the application of (3·1·2) or (3·2·2) with choices of indices which take full advantage of the space-group symmetry. The final step is in the form of a general application which is the same for all the space groups.

The specification of the origin is carried out in conformance with the seminvariant theory previously developed (Hauptman & Karle, 1953, 1959). It is the same for all space groups of a given type, and therefore is the same for all the space groups considered here.

In type $3P_2$, the phases φ_{hkl} which are structure seminvariants, are of the form $h+k+l \equiv 0 \pmod 2$. In other words either one or all three of the indices must be even. This means that once the functional form of the structure factor has been chosen, the values of these phases are uniquely determined by the intensities alone. It is of interest to note in the procedures to follow, how a single equation, (3·1·2) or (3·2·2), used in conjunction with relationships among the structure factors, characteristic of the particular space group and the chosen functional form for the structure factor, does, in fact, lead to unique values for the structure seminvariants.

4·1. *Rhombohedral system*

We are concerned here with space groups $R\bar{3}$, $R\bar{3}m$ and $R\bar{3}c$.* Two special choices of $\mathbf{h}_1$ and $\mathbf{h}_2$, in addition to $\mathbf{h}_1=\mathbf{h}_2$, are shown in the first two rows of Table 1. By means of the first of these choices,

$$\mathbf{h}_1=(h_1,\ \bar{h}+h_1,\ l+h_1) \quad \text{and} \quad \mathbf{h}_2=(h+\bar{h}_1,\ \bar{l}+\bar{h}_1,\ \bar{h}_1)\ ,$$

equation (3·1·2) or (3·2·2) yields the value of $\mathscr{E}'^2_{h_1,\bar{h}+h_1,l+h_1}\mathscr{E}'_{hkl}$, from which $\varphi'_{hkl}(h+k+l=0)$ may be determined. The second choice of $\mathbf{h}_1$ and $\mathbf{h}_2$ used with (3·1·2) or (3·2·2) yields the value of

$$\mathscr{E}'^2_{1/2(h+\bar{k}+l),\,1/2(h+k+\bar{l}),\,1/2(\bar{h}+k+l)}\mathscr{E}'_{hkl}\ ,$$

from which $\varphi'_{hkl}(h+k+l \equiv 0 \pmod 2)$ may be determined. Additional choices for $R\bar{3}m$ and $R\bar{3}c$ appear in Table 2. For example, the first pair of $\mathbf{h}_1$ and $\mathbf{h}_2$ in column 2 yields the value of $\mathscr{E}'^2_{h_1,\bar{h}+h_1,l}\mathscr{E}_{h\bar{h}0}$ multiplied by the numerical coefficient given in column 2 of Table 2. For $R\bar{3}c$, the relationship

$$\mathscr{E}'_{hkl}=(-1)^{h+k+l}\mathscr{E}'_{khl}\ ,$$

following from the chosen functional form for the structure factor, gives rise to the entry $(-1)^{h+l_1}$ in column 2. In this way the value of the phase $\varphi'_{h\bar{h}0}$ is determined. The remaining choices for $\mathbf{h}_1$ and $\mathbf{h}_2$ of Table 2 yield, in a similar way, the values of φ'_{hh2l}, $\varphi'_{i\bar{i}0l}$, φ'_{l2kl}, $\varphi'_{0k\bar{k}}$, and φ'_{2hkk}. The entries in this

* The discussion to follow is equally valid for the supergroups included in Tables 1, 2 and 3.

Table 1

Two choices of $\mathbf{h}_1$ and $\mathbf{h}_2$ for obtaining seminvariant phases for space groups, $R\bar{3}$, $R\bar{3}m$, $R\bar{3}c$, $Pm3$, $Pn3$, $Pa3$, $Pm3m$, $Pn3n$, $Pm3n$, $Pn3m$, $Fm3$, $Fd3$, $Fm3m$, $Fm3c$, $Fd3m$ and $Fd3c$, by means of (3·1·2) or (3·2·2). The latter equations yield the value of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ from which the value of $\varphi'_{\mathbf{h}}$ may be inferred.

$\mathbf{h}_1$	h_1,	$\bar{h}+h_1$,	$l+h_1$	$\frac{1}{2}(h+\bar{k}+l)$,	$\frac{1}{2}(h+k+\bar{l})$,	$\frac{1}{2}(\bar{h}+k+l)$
$\mathbf{h}_2$	$h+h_1$,	$\bar{l}+\bar{h}_1$,	$\bar{h}_1$	$\frac{1}{2}(h+k+\bar{l})$,	$\frac{1}{2}(\bar{h}+k+l)$,	$\frac{1}{2}(h+\bar{k}+l)$
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	h,	k,	l	h,	k,	l
Condition	$h+k+l=0$			$h+k+l \equiv 0 \pmod 2$		

Table 2

The coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ given by the left side of (3·1·2) or (3·2·2), for selected values of $\mathbf{h}_1$ and $\mathbf{h}_2$, and for each of six space groups. The notation $P(Fm3m)$ refers to the primitive unit cell, instead of the conventionally centered one (cf. Hauptman & Karle, 1959)

$\mathbf{h}_1$	h_1,	$\bar{h}+h_1$,	l_1	h_1,	$h+\bar{h}_1$,	l	$\bar{l}+l_1$,	k_1,	l_1	$l+\bar{l}_1$,	k,	l_1	h_1,	k_1,	$\bar{k}+k_1$	h,	k_1,	$k+\bar{k}_1$
$\mathbf{h}_2$	$h+\bar{h}_1$,	$\bar{h}_1$,	l_1	$h+\bar{h}_1$,	h_1,	l	l_1,	$\bar{k}_1$,	$l+l_1$	l_1,	k,	$l+l_1$	$\bar{h}_1$,	$k+\bar{k}_1$,	$\bar{k}_1$	h,	$k+\bar{k}_1$,	k_1
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	h,	$\bar{h}$,	0	h,	h,	$2l$	$\bar{l}$,	0	l	l,	$2k$,	l	0,	k,	$\bar{k}$	$2h$,	k,	k
$R\bar{3}m$																		
$P(Fm3m)$		$+1$			$+1$			$+1$			$+1$			$+1$			$+1$	
$P(Fd3m)$																		
$R\bar{3}c$																		
$P(Fm3c)$		$(-1)^{h+l_1}$			$(-1)^{h+l}$			$(-1)^{l+k_1}$			$(-1)^{l+k}$			$(-1)^{k+h_1}$			$(-1)^{k+h}$	
$P(Fd3c)$																		

table are the coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ which occur on the left side of (3·1·2) or (3·2·2). In general h_1, k_1 and l_1 in Tables 1 and 2 may be chosen arbitrarily, permitting the possible use of many combinations of $\mathbf{h}_1$ and $\mathbf{h}_2$ for obtaining the value of a particular phase. As always, the computations are performed for the larger values of $|\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}|$.

We note that the phases obtained from Tables 1 and 2 are phases $\varphi'_{hkl}(h+k+l \equiv 0 \pmod 2)$, which are seminvariants. By use of these, it is possible to calculate the values of additional seminvariants as illustrated by typical examples in Table 3. It is to be noted that (3·1·2) or (3·2·2) now yields the value of $\mathscr{E}'_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}_2}\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}$ where $\mathscr{E}'_{\mathbf{h}_1}$ and $\mathscr{E}'_{\mathbf{h}_2}$ are assumed to have been found by use of Tables 1 and 2. Again h_1, k_1 and l_1 are arbitrary, but limited by the set of previously determined phases.

For the purpose of specifying the origin a linearly semi-independent phase, $\varphi'_\alpha = \varphi'_{hkl}(h+k+l \not\equiv 0 \pmod 2)$, having a large corresponding $|\mathscr{E}'_{hkl}|$ is chosen. The value (0 or π) of φ'_α is then specified arbitrarily, thus fixing the origin. Systematic application of equation (3·1·2) or (3·2·2) then permits the determination of the phases $\varphi'_{\mathbf{h}}$ of the remaining $\mathscr{E}'_{\mathbf{h}}$ of interest, using previously determined or specified phases as necessary.

An example of a linearly semi-independent phase is φ_{ggu} ($g \equiv$ even, $u \equiv$ odd). We recall that phases of the type φ_{ggg}, φ_{guu}, φ_{ugu}, and φ_{uug} may be obtained directly from the intensities before an origin specification has been made. From the specified phase and previously determined phases, additional phases are obtainable by suitable choices of $\mathbf{h}_1$ and $\mathbf{h}_2$ in (3·1·2) or (3·2·2). It is readily seen that any phase is accessible, once the origin specification has been made. This follows

Table 3

Examples of $\mathbf{h}_1$ and $\mathbf{h}_2$ which may be inserted into (3·1·2) or (3·2·2) in order to obtain the product $\mathscr{E}'_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}_2}\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}$ from which the values of additional seminvariant phases may be inferred. This requires a knowledge of $\varphi'_{\mathbf{h}_1}$ and $\varphi'_{\mathbf{h}_2}$ which may be obtained by use of Table 2. Thus, this list has a particular significance for the six space groups included in Table 2. The entries may undergo cyclic permutation on h, k, l

$\mathbf{h}_1$	h_1,	$\bar{h}+k+h_1$,	$h+\bar{k}+2\bar{h}_1$	$h+\bar{l}$,	$\bar{h}+l$,	0	$k+2\bar{k}_1$,	$k+2\bar{k}_1$,	$\bar{h}+k+l+2\bar{k}_1$	$2h_1$,	$\bar{h}+k+2h_1$,	$2l_1$
$\mathbf{h}_2$	$h+\bar{h}_1$,	$h+\bar{h}_1$,	$\bar{h}+k+l+2h_1$	l,	$h+k+\bar{l}$,	l	$h+\bar{k}+2k_1$,	$2k_1$,	$h+\bar{k}+2k_1$	$h+2\bar{h}_1$,	$h+2\bar{h}_1$,	$2l+2\bar{l}_1$
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	h,	k,	l	h,	k,	l	h,	k,	l	h,	k,	$2l$
				$h+k+l \equiv 0 \pmod 2$						$h \equiv k \pmod 2$		

Table 4

The coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}_2}$ given by the left side of (3·1·2) or (3·2·2), for selected values of $\mathbf{h}_1$ and $\mathbf{h}_2$, and for each of seven space groups. The entries may undergo cyclic permutation on h, k, l

$\mathbf{h}_1$	h,	k_1,	l_1	h_1,	k,	l	h_1,	$h+\bar{h}_1$,	$l+\bar{h}_1$	$\frac{1}{2}(h+k+l)$,	$\frac{1}{2}(\bar{h}+k+\bar{l})$,	$\frac{1}{2}(\bar{h}+k+l)$
$\mathbf{h}_2$	h,	$\bar{k}_1$,	$\bar{l}_1$	$\bar{h}_1$,	k,	l	$h+\bar{h}_1$,	$l+h_1$,	h_1	$\frac{1}{2}(h+\bar{k}+\bar{l})$,	$\frac{1}{2}(h+k+l)$,	$\frac{1}{2}(h+\bar{k}+l)$
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	$2h$,	0,	0	0,	$2k$,	$2l$	h,	k,	l	h,	k,	l
							$-h+k+l=0$			$h+k+l \equiv 0 \pmod 2$		
$Pm3$												
$Pm3m$		$+1$			$+1$			$+1$			$+1$	
$Pm3n$												
$Pn3$												
$Pn3m$		$(-1)^{k_1+l_1}$			$(-1)^{k+l}$			$(-1)^h$			$(-1)^l$	
$Pn3n$												
$Pa3$		$(-1)^{h+k_1}$			$(-1)^{h_1+k}$			$(-1)^l$			$(-1)^k$	

Table 5

The coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ given by the left side of (3·1·2) or (3·2·2), for selected values of $\mathbf{h}_1$ and $\mathbf{h}_2$, and for each of four space groups. The entries may undergo cyclic permutation on h, k, l

$\mathbf{h}_1$	$\frac{1}{2}(h+k)$,	$\frac{1}{2}(\bar{h}+k)$,	l_1	$\frac{1}{2}(h+k)$,	$\frac{1}{2}(\bar{h}+k)$,	l	h_1,	$h+\bar{h}_1$,	l_1	h_1,	$\bar{h}+h_1$,	l_1	h_1,	$h+\bar{h}_1$,	l	h_1,	$\bar{h}+h_1$,	l
$\mathbf{h}_2$	$\frac{1}{2}(h+\bar{k})$,	$\frac{1}{2}(h+k)$,	$\bar{l}_1$	$\frac{1}{2}(h+\bar{k})$,	$\frac{1}{2}(h+k)$,	l	$h+\bar{h}_1$,	h_1,	$\bar{l}_1$	$h+\bar{h}_1$,	$\bar{h}_1$,	$\bar{l}_1$	$h+\bar{h}_1$,	h_1,	l	$h+\bar{h}_1$,	$\bar{h}_1$,	l
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	h,	k,	0	h,	k,	$2l$	h,	h,	0	h,	$\bar{h}$,	0	h,	h,	$2l$	h,	$\bar{h}$,	$2l$
	$h \equiv k \pmod 2$			$h \equiv k \pmod 2$														
$Pm3m$	$+1$			$+1$			$+1$			$+1$			$+1$			$+1$		
$Pn3n$	$(-1)^{\frac{1}{2}(h+k)}$			$(-1)^{\frac{1}{2}(h-k)}$			$(-1)^{l_1}$			$(-1)^{h+l_1}$			$(-1)^{h+l}$			$(-1)^l$		
$Pm3n$	$(-1)^{k+l_1}$			$(-1)^{k+l}$			$(-1)^{h+l_1}$			$(-1)^{h+l_1}$			$(-1)^{h+l}$			$(-1)^{h+l}$		
$Pn3m$	$(-1)^{\frac{1}{2}(h-k)+l_1}$			$(-1)^{\frac{1}{2}(h+k)+l}$			$(-1)^h$			$+1$			$+1$			$(-1)^h$		

from the fact that, starting with the specified phases and those of the form φ'_{hkl} ($h+k+l \equiv 0 \pmod 2$), it is possible to express an arbitrary vector $\mathbf{h}$ (whose components have any parity) in the form $\mathbf{h}_1+\mathbf{h}_2$, where $\varphi'_{\mathbf{h}_1}$ and $\varphi'_{\mathbf{h}_2}$ are known. For example, $\varphi'_h=\varphi'_{gug}$ is obtainable from suitable phases $\varphi'_{\mathbf{h}_1}=\varphi'_{ggu}$ and $\varphi'_{\mathbf{h}_2}=\varphi'_{guu}$ where $\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$. The remaining types φ'_{ugg} and φ'_{uuu} are similarly obtained.

4·2. *Cubic system, primitive*

We are concerned here with the seven space groups, $Pm3$, $Pn3$, $Pa3$, $Pm3m$, $Pn3n$, $Pm3n$ and $Pn3m$. The special choices for $\mathbf{h}_1$ and $\mathbf{h}_2$ are shown in the first two rows of Tables 1, 4 and 5. Table 1 has been described in § 4·1. The entries in Tables 4 and 5 are the coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ which occur on the left side of (3·1·2) or (3·2·2). Again the h_1, k_1 and l_1 in the tables may be chosen arbitrarily, permitting the possible use of many combinations of $\mathbf{h}_1$ and $\mathbf{h}_2$ for obtaining the value of a particular phase. In the application of Tables 4 and 5, the entries in each of the columns may be carried through cyclic permutations on the h, k and l, which would multiply the number of possible choices by three. For example, the cyclic permutations are carried out in detail in Table 2, wherein columns 4 and 6 are cyclic permutations of column 2 and columns 5 and 7 are cyclic permutations of column 3. In a manner analogous to that illustrated by Table 3, it is possible to use phases obtained by means of Tables 4 and 5 to obtain additional phases which are seminvariants. Finally, the origin is specified as in § 4·1 and the phase determination is completed.

4·3. *Cubic system, F-centered*

We are concerned here with the six space groups, $Fm3$, $Fd3$, $Fm3m$, $Fm3c$, $Fd3m$ and $Fd3c$. The special choices for $\mathbf{h}_1$ and $\mathbf{h}_2$ are shown in the first two rows of Tables 1, 2, 6 and 7. The notation $P(Fm3)$ implies that the space group $Fm3$ is referred to the primitive unit cell defined previously (Hauptman & Karle, 1959). Tables 1 and 2 have been described in § 4·1. The entries in Tables 6 and 7 are the coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ which occur on the left side of (3·1·2) or (3·2·2). Again the h_1, k_1 and l_1 in the tables may be chosen arbitrarily, permitting the possible use of many combinations of $\mathbf{h}_1$ and $\mathbf{h}_2$ for obtaining the value of a particular phase. In the application of Tables 6 and 7, the entries in each of the columns may be carried through cyclic permutations on the h, k and l, which would multiply the number of possible choices by three (cf. Tables 2 and 8, where the cyclic permutations are explicitly carried out). In a manner analogous to that illustrated by Table 3, it is possible to use phases obtained by means of Tables 6 and 7 to obtain additional phases which are seminvariants. Finally, the origin is specified as in § 4·1 and the phase determination is completed.

Table 6

The coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ given by the left side of (3·1·2) or (3·2·2), for selected values of $\mathbf{h}_1$ and $\mathbf{h}_2$, and for each of six space groups. The entries may undergo cyclic permutation on h, k, l

$\mathbf{h}_1$	$h_1,\ k_1,\ \bar{h}+h_1+k_1$	$h_1,\ k+\bar{l}+h_1,\ l$	$\bar{l}+h,\ l,\ l_1$	$k,\ \bar{h}+k,\ \frac{1}{2}(\bar{h}+k+l)$
$\mathbf{h}_2$	$h+\bar{h}_1,\ h+\bar{k}_1,\ h+\bar{h}_1+\bar{k}_1$	$h+\bar{h}_1,\ l+\bar{h}_1,\ l$	$l,\ k+\bar{l},\ l+\bar{l}_1$	$h+\bar{k},\ h,\ \frac{1}{2}(h+\bar{k}+l)$
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	$h,\ h,\ 0$	$h,\ k,\ 2l$	$h,\ k,\ l$	$h,\ k,\ l$
		$2l=h+k$	$h+k-3l=0$	$h+k+l \equiv 0 \pmod 2$
$P(Fm3)$				
$P(Fm3m)$	$+1$	$+1$	$+1$	$+1$
$P(Fm3c)$				
$P(Fd3)$				
$P(Fd3m)$	$(-1)^{h+h_1+k_1}$	$(-1)^l$	$(-1)^l$	$(-1)^{h+k}$
$P(Fd3c)$				

Table 7

The coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ given by the left side of (3·1·2) or (3·2·2), for selected values of $\mathbf{h}_1$ and $\mathbf{h}_2$, and for each of four space groups. The entries may undergo cyclic permutation on h, k, l

$\mathbf{h}_1$	$h,\ k_1,\ l_1$	$h_1,\ \frac{1}{2}(k+h_1),\ \frac{1}{2}(l+h_1)$	$\frac{1}{4}(h+k+l),\ \frac{1}{4}(\bar{h}+3k+\bar{l}),\ \frac{1}{2}(\bar{h}+k+l)$	$h_1,\ k+h_1,\ h$
$\mathbf{h}_2$	$h,\ h+\bar{k}_1,\ h+\bar{l}_1$	$\bar{h}_1,\ \frac{1}{2}(k+\bar{h}_1),\ \frac{1}{2}(l+\bar{h}_1)$	$\frac{1}{4}(3h+\bar{k}+\bar{l}),\ \frac{1}{4}(h+k+l),\ \frac{1}{2}(h+\bar{k}+l)$	$h+\bar{h}_1,\ \bar{h}_1,\ k$
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	$2h,\ h,\ h$	$0,\ k,\ l$	$h,\ k,\ l$	$h,\ k,\ h+k$
		$h_1 \equiv k \equiv l \pmod 2$	$h+k+l \equiv 0 \pmod 4$	
$P(Fm3m)$	$+1$	$+1$	$+1$	$+1$
$P(Fm3c)$	$(-1)^{h+k_1+l_1}$	$(-1)^{\frac{1}{2}(k+l)}$	$(-1)^l$	$(-1)^{h+k}$
$P(Fd3m)$	$(-1)^h$	$(-1)^{h_1}$	$(-1)^{\frac{1}{4}(h+k+l)}$	$(-1)^{h_1}$
$P(Fd3c)$	$(-1)^{k_1+l_1}$	$(-1)^{\frac{1}{2}(k+l+2h_1)}$	$(-1)^{\frac{1}{4}(h+k-2l)}$	$(-1)^{h+k+h_1}$

Table 8

The coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ given by the left side of (3·1·2) or (3·2·2), for selected values of $\mathbf{h}_1$ and $\mathbf{h}_2$, and for each of two space groups

$\mathbf{h}_1$	h_1,	k_1,	$\bar{h}+h_1+k_1$	$\bar{k}+k_1+l_1$,	k_1,	l_1	h_1,	$\bar{l}+h_1+l_1$,	l_1	h,	k_1,	$\bar{h}+l+k_1$	$h+\bar{k}+l_1$,	k,	l_1	h_1,	$k+\bar{l}+h_1$,	l
$\mathbf{h}_2$	$h+\bar{h}_1$,	$h+\bar{k}_1$,	$h+\bar{h}_1+\bar{k}_1$	$k+\bar{k}_1+\bar{l}_1$,	$k+\bar{k}_1$,	$k+\bar{l}_1$	$l+\bar{h}_1$,	$l+\bar{h}_1+\bar{l}_1$,	$l+\bar{l}_1$	$h, k+\bar{k}_1$,		$h+\bar{k}_1$	$k+\bar{l}_1$,	k,	$l+\bar{l}_1$	$h+\bar{h}_1$,	$l+\bar{h}_1$,	l
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	h,	h,	0	0,	k,	k	l,	0,	l	$2h$,	k,	l	h,	$2k$,	l	h,	$2k$,	$2l$
										$2h=k+l$			$2k=h+l$			$2l=h+k$	
$P(Fmmm)$			$+1$		$+1$			$+1$				$+1$			$+1$			$+1$
$P(Fddd)$			$(-1)^{h+h_1+k_1}$		$(-1)^{k+k_1+l_1}$			$(-1)^{l+h_1+l_1}$				$(-1)^h$			$(-1)^k$			$(-1)^l$

Table 9

Examples of $\mathbf{h}_1$ and $\mathbf{h}_2$ which may be inserted into (3·1·2) or (3·2·2) in order to obtain the product $\mathscr{E}'_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}_2}\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}$, from which the values of additional seminvariant phases may be inferred. This requires a knowledge of phases previously obtained from use of Table 8 and thus has a particular significance for the two space groups listed there. The entries may undergo cyclic permutation on h, k, l

$\mathbf{h}_1$	$h, h, 0$	$\frac{1}{2}(h+k+\bar{l})$,	k, $\frac{1}{2}(\bar{h}+k+l)$
$\mathbf{h}_2$	$0, l, l$	$\frac{1}{2}(h+\bar{k}+l)$,	0, $\frac{1}{2}(h+\bar{k}+l)$
$\mathbf{h}=\mathbf{h}_1+\mathbf{h}_2$	h, k, l	h,	k, l
Conditions	$h-k+l=0$	$h+k+l \equiv 0 \pmod 2$	

4·4. *Orthorhombic system, F-centered*

We are concerned here with the two space groups *Fmmm* and *Fddd*. The special choices for $\mathbf{h}_1$ and $\mathbf{h}_2$ are shown in the first two rows of Table 8. The entries in Table 8 are the coefficients of $\mathscr{E}'^2_{\mathbf{h}_1}\mathscr{E}'_{\mathbf{h}}$ which occur on the left side of (3·1·2) or (3·2·2). We note that columns 3 and 4 are cyclic permutations of column 2. Table 9 illustrates how additional seminvariants may be obtained from the results from Table 8. For example, column 2 of Table 9 utilizes the results of columns 2 and 4 of Table 8; and column 3 of Table 9 utilizes the results of column 4 of Table 8 and column 2 of Table 9 in order to obtain new phases. Finally, the origin is specified as in § 4·1 and the phase determination is completed.

5. Concluding remarks

This paper should be read in conjunction with *1P* (1959), in which the symbols are defined and general remarks are made which are applicable to all the space groups.

The main choices of $\mathbf{h}_1$ and $\mathbf{h}_2$ for the various space groups are listed in the tables. They illustrate how the seminvariant phases can be obtained directly from the X-ray intensities in many different ways.

The many ways of calculating a particular phase, together with the fact that the calculation of the right sides of (3·1·2) and (3·2·2) should yield not only the sign of the left side, but also its magnitude, serves as a good internal consistency check as the phase determination proceeds. It is important to bear in mind that the λ's or Λ's derived from one and two-dimensional data for crystals having considerable overlap in projection may make incorrect contributions to (3·1·2) and (3·2·2). Overlap in a projection results in a reduction of the effective number of atoms in that projection, a factor which is not taken into account in the derivation of (3·1·2) and (3·2·2). It may therefore often prove worthwhile to calculate (3·1·2) and (3·2·2), using only those λ's and Λ's which are derived from three-dimensional data.

6. Appendix

The correction terms for the formulas listed in § 3 are given here and in $1P$ (1959). As a general rule, for larger N, these terms make a very small contribution. In any specific instance, the investigator can judge their importance for himself.

We define:

$$\underline{{}_9R_{2,\,0}} = -\frac{\sigma_8^{1/2}}{\sigma_4}(\mathscr{E}'''_{2h00}+\mathscr{E}'''_{02k0}+\mathscr{E}'''_{002l}) + \frac{4\sigma_6}{\sigma_2\sigma_4}(p+q-4)+\varrho_1, \tag{6·1}$$

where,

$$\varrho_1 = -\frac{2\sigma_8^{1/2}}{\sigma_2\sigma_4^{1/2}}(p+q-4)\mathscr{E}'_{\mathbf{h}}\mathscr{E}'''_{\mathbf{h}} - \frac{\sigma_4}{4\sigma_2^2}((p-2)(p-4)+(q-2)(q-4))\mathscr{E}'^2_{\mathbf{h}} + \frac{\sigma_4}{16\sigma_2^2}((p-2)(q-2)+2(p-2)(p-4) +2(q-2)(q-4))+\ldots, \tag{6·2}$$

$$\underline{{}_{10}R_{2,\,0}} = \varrho_2+\varrho_3, \tag{6·3}$$

where,

$$\varrho_2 = -\frac{\sigma_8^{1/2}}{\sigma_4}(3\mathscr{E}'''_{2h00}+3\mathscr{E}'''_{02k0}+3\mathscr{E}'''_{002l}+\mathscr{E}'''_{h+\bar{k},h+\bar{k},0} + \mathscr{E}'''_{0,k+\bar{l},k+\bar{l}}+\mathscr{E}'''_{h+\bar{l},0,h+\bar{l}}+\mathscr{E}'''_{h+k,h+k,0}+\mathscr{E}'''_{0,k+l,k+l} + \mathscr{E}'''_{h+l,0,h+l}+2\mathscr{E}'''_{h+k,\bar{h}+k,0}+2\mathscr{E}'''_{0,k+\bar{l},k+l} +2\mathscr{E}'''_{h+l,0,\bar{h}+l}), \tag{6·4}$$

and,

$$\varrho_3 = -\frac{14\sigma_8^{1/2}}{\sigma_2\sigma_4^{1/2}}(p+q-4)\mathscr{E}'_{\mathbf{h}}\mathscr{E}'''_{\mathbf{h}} - \frac{7\sigma_4}{4\sigma_2^2}((p-2)(p-4)+(q-2)(q-4))\mathscr{E}'^2_{\mathbf{h}} + \frac{49\sigma_6}{\sigma_2\sigma_4}(p+q-4)+\frac{7\sigma_4}{16\sigma_2^2}((p-2)(q-2) +2(p-2)(p-4)+2(q-2)(q-4))+\ldots, \tag{6·5}$$

$$\underline{{}_{11}R_{2,\,0}} = -\frac{\sigma_8^{1/2}}{\sigma_4}(\mathscr{E}'''_{0,\bar{h}+k+l,\bar{h}+k+l}+\mathscr{E}'''_{h+\bar{k}+l,0,h+\bar{k}+l} + \mathscr{E}'''_{h+k+\bar{l},h+k+\bar{l},0})+\frac{4\sigma_6}{\sigma_2\sigma_4}(p+q-4)+\varrho_1, \tag{6·6}$$

$$\underline{{}_{12}R_{2,\,0}} = \varrho_3+\varrho_4, \tag{6·7}$$

where,

$$\varrho_4 = -\frac{\sigma_8^{1/2}}{\sigma_4}(3\mathscr{E}'''_{0,\bar{h}+k+l,\bar{h}+k+l}+3\mathscr{E}'''_{h+\bar{k}+l,0,h+\bar{k}+l} +3\mathscr{E}'''_{h+k+\bar{l},h+k+\bar{l},0}+\mathscr{E}'''_{2h,h,h}+\mathscr{E}'''_{k,2k,k}+\mathscr{E}'''_{l,l,2l} +\mathscr{E}'''_{h+\bar{k},\bar{h}+k,0}+\mathscr{E}'''_{0,k+\bar{l},\bar{k}+l}+\mathscr{E}'''_{h+\bar{l},0,\bar{h}+l} +\mathscr{E}'''_{l,\bar{h}+k,\bar{h}+k+l}+\mathscr{E}'''_{h+\bar{k}+l,h,\bar{k}+l}+\mathscr{E}'''_{h+\bar{l},h+k+\bar{l},k}), \tag{6·8}$$

$$\underline{{}_{13}R_{2,\,0}} = -\frac{!\sigma_8^{1/2}}{\sigma_4}(\mathscr{E}'''_{0,\bar{h}+k+l,\bar{h}+k+l}+\mathscr{E}'''_{h+\bar{k}+l,0,h+\bar{k}+l} +\mathscr{E}'''_{h+k+\bar{l},h+k+\bar{l},0})+\frac{2\sigma_6}{\sigma_2\sigma_4}(p+q-4)+\varrho_1, \tag{6·9}$$

$$\underline{{}_9R_{3,\,0}} = -\frac{\sigma_4^{1/2}}{8\sigma_2}((r-2)\mathscr{E}'^2_{\mathbf{h}_1} +(p-2)\mathscr{E}'^2_{\mathbf{h}_2}+(q-2)\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_5, \tag{6·10}$$

where

$$\varrho_5 = -\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_1}(\mathscr{E}'''_{h_1+2h_2,k_1,l_1}+\mathscr{E}'''_{h_1,k_1+2k_2,l_1} +\mathscr{E}'''_{h_1,k_1,l_1+2l_2}) -\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_2}(\mathscr{E}'''_{2h_1+h_2,k_2,l_2}+\mathscr{E}'''_{h_2,2k_1+k_2,l_2} +\mathscr{E}'''_{h_2,k_2,2l_1+l_2}) -\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}(\mathscr{E}'''_{h_1+\bar{h}_2,k_1+k_2,l_1+l_2}+\mathscr{E}'''_{h_1+h_2,k_1+\bar{k}_2,l_1+l_2} +\mathscr{E}'''_{h_1+h_2,k_1+k_2,l_1+\bar{l}_2})+\ldots, \tag{6·11}$$

$$\underline{{}_{10}R_{3,\,0}} = -\frac{7\sigma_4^{1/2}}{8\sigma_2}((r-2)\mathscr{E}'^2_{\mathbf{h}_1} +(p-2)\mathscr{E}'^2_{\mathbf{h}_2}+(q-2)\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_6, \tag{6·12}$$

where,

$$\varrho_6 = -\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_1}(3\mathscr{E}'''_{h_1+2h_2,k_1,l_1}+3\mathscr{E}'''_{h_1,k_1+2k_2,l_1} +3\mathscr{E}'''_{h_1,k_1,l_1+2l_2}+\mathscr{E}'''_{h_1+h_2+\bar{k}_2,h_2+\bar{k}_1+\bar{k}_2,l_1} +\mathscr{E}'''_{h_1+h_2+k_2,h_2+k_1+k_2,l_1}+\mathscr{E}'''_{h_1+h_2+\bar{k}_2,h_2+k_1+k_2,l_1} +\mathscr{E}'''_{h_2+\bar{k}_1+\bar{k}_2,h_1+h_2+k_2,l_1}+\mathscr{E}'''_{h_1,\bar{k}_1+\bar{k}_2+l_2,\bar{k}_2+l_1+l_2} +\mathscr{E}'''_{h_1,k_1+k_2+l_2,k_2+l_1+l_2}+\mathscr{E}'''_{h_1,k_1+k_2+l_2,\bar{k}_2+l_1+l_2} +\mathscr{E}'''_{h_1,k_2+l_1+l_2,\bar{k}_1+\bar{k}_2+l_2}+\mathscr{E}'''_{h_1+h_2+\bar{l}_2,k_1,h_2+\bar{l}_1+\bar{l}_2} +\mathscr{E}'''_{h_1+h_2+l_2,k_1,h_2+l_1+l_2}+\mathscr{E}'''_{h_1+h_2+\bar{l}_2,k_1,h_2+l_1+l_2} +\mathscr{E}'''_{h_2+\bar{l}_1+\bar{l}_2,k_1,h_1+h_2+l_2}) -\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_2}(3\mathscr{E}'''_{2h_1+h_2,k_2,l_2}+3\mathscr{E}'''_{h_2,2k_1+k_2,l_2} +3\mathscr{E}'''_{h_2,k_2,2l_1+l_2}+\mathscr{E}'''_{h_1+h_2+\bar{k}_1,\bar{h}_1+k_1+k_2,l_2} +\mathscr{E}'''_{h_1+k_1+k_2,h_1+h_2+k_1,l_2}+\mathscr{E}'''_{h_1+h_2+\bar{k}_1,h_1+k_1+k_2,l_2} +\mathscr{E}'''_{h_1+h_2+k_1,\bar{h}_1+k_1+k_2,l_2}+\mathscr{E}'''_{h_2,k_1+k_2+\bar{l}_1,\bar{k}_1+l_1+l_2} +\mathscr{E}'''_{h_2,k_1+l_1+l_2,k_1+k_2+l_1}+\mathscr{E}'''_{h_2,k_1+k_2+l_1,\bar{k}_1+l_1+l_2} +\mathscr{E}'''_{h_2,k_1+k_2+\bar{l}_1,k_1+l_1+l_2}+\mathscr{E}'''_{h_1+h_2+\bar{l}_1,k_2,\bar{h}_1+l_1+l_2} +\mathscr{E}'''_{h_1+l_1+l_2,k_2,h_1+h_2+l_1}+\mathscr{E}'''_{h_1+h_2+\bar{l}_1,k_2,h_1+l_1+l_2} +\mathscr{E}'''_{h_1+h_2+l_1,k_2,\bar{h}_1+l_1+l_2}) -\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}(3\mathscr{E}'''_{h_1+\bar{h}_2,k_1+k_2,l_1+l_2} +3\mathscr{E}'''_{h_1+h_2,k_1+\bar{k}_2,l_1+l_2}+3\mathscr{E}'''_{h_1+h_2,k_1+k_2,l_1+\bar{l}_2} +\mathscr{E}'''_{h_2+k_1,h_1+k_2,l_1+l_2}+\mathscr{E}'''_{h_2+\bar{k}_1,\bar{h}_1+k_2,l_1+l_2} +\mathscr{E}'''_{h_1+\bar{k}_2,h_2+k_1,l_1+l_2}+\mathscr{E}'''_{h_2+\bar{k}_1,h_1+k_2,l_1+l_2}$$

$$+\mathscr{E}'''_{h_1+h_2,\,k_2+l_1,\,k_1+l_2}+\mathscr{E}'''_{h_1+h_2,\,k_2+\bar{l}_1,\,\bar{k}_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2,\,k_1+l_2,\,\bar{k}_2+l_1}+\mathscr{E}'''_{h_1+h_2,\,k_2+l_1,\,\bar{k}_1+l_2}$$
$$+\mathscr{E}'''_{h_2+l_1,\,k_1+k_2,\,h_1+l_2}+\mathscr{E}'''_{h_2+\bar{l}_1,\,k_1+k_2,\,\bar{h}_1+l_2}$$
$$+\mathscr{E}'''_{h_1+\bar{l}_2,\,k_1+k_2,\,h_2+l_1}+\mathscr{E}'''_{h_2+\bar{l}_1,\,k_1+k_2,\,h_1+l_2})+\ldots\,, \tag{6·13}$$

$$\underline{{}_{11}R_{3,\,0}}=-\frac{\sigma_4^{1/2}}{8\sigma_2}((r-2)\mathscr{E}'^2_{\mathbf{h}_1}+(p-2)\mathscr{E}'^2_{\mathbf{h}_2}+(q-2)$$
$$\times\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_7\,, \tag{6·14}$$

where

$$\varrho_7=-\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_1}(\mathscr{E}'''_{h_1,\,\bar{h}_2+k_1+k_2+l_2,\,\bar{h}_2+k_2+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{k}_2+l_2,\,k_1,\,h_2+\bar{k}_2+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+k_2+\bar{l}_2,\,h_2+k_1+k_2+\bar{l}_2,\,l_1})$$
$$-\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_2}(\mathscr{E}'''_{h_2,\,\bar{h}_1+k_1+k_2+l_1,\,\bar{h}_1+k_1+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+k_1+\bar{l}_1,\,h_1+k_1+k_2+\bar{l}_1,\,l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{k}_1+l_1,\,k_2,\,h_1+\bar{k}_1+l_1+l_2})$$
$$-\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2},(\mathscr{E}'''_{h_1+h_2,\,h_1+k_2+\bar{l}_1,\,h_1+\bar{k}_1+l_2}$$
$$+\mathscr{E}'''_{h_2+k_1+\bar{l}_1,\,k_1+k_2,\,\bar{h}_1+k_1+l_2}$$
$$+\mathscr{E}_{h_2+\bar{k}_1+l_1,\,\bar{h}_1+k_2+l_1,\,l_1+l_2})+\ldots\,, \tag{6·15}$$

$$\underline{{}_{12}R_{3,\,0}}=-\frac{7\sigma_4^{1/4}}{8\sigma_2}((r-2)\mathscr{E}'^2_{\mathbf{h}_1}+(p-2)\mathscr{E}'^2_{\mathbf{h}_2}+(q-2)$$
$$\times\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_8\,, \tag{6·16}$$

where,

$$\varrho_8=-\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}_{\mathbf{h}_1}(3\mathscr{E}''_{h_1,\,\bar{h}_2+k_1+k_2+l_2,\,\bar{h}_2+k_2+l_1+l_2}$$
$$+3\mathscr{E}'''_{h_1+h_2+\bar{k}_2+l_2,\,k_1,\,h_2+\bar{k}_2+l_1+l_2}$$
$$+3\mathscr{E}'''_{h_1+h_2+k_2+\bar{l}_2,\,h_2+k_1+k_2+\bar{l}_2,\,l_1}$$
$$+\mathscr{E}'''_{h_1+l_2,\,\bar{h}_2+k_1+k_2,\,\bar{h}_2+k_2+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{k}_2,\,k_1+l_2,\,h_2+\bar{k}_2+l_1+l_2}+\mathscr{E}'''_{h_1+l_2,\,k_1+l_2,\,l_1+2l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{k}_2,\,\bar{h}_2+k_1+k_2,\,l_1}+\mathscr{E}'''_{h_1+h_2+\bar{k}_2+l_2,\,h_2+k_1,\,\bar{k}_2+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{l}_2,\,h_2+k_1+k_2+\bar{l}_2,\,k_2+l_1}$$
$$+\mathscr{E}'''_{h_1+h_2+k_2+\bar{l}_2,\,k_1+k_2+\bar{l}_2,\,h_2+l_1}$$
$$+\mathscr{E}'''_{h_1+k_2,\,\bar{h}_2+k_1+k_2+l_2,\,\bar{h}_2+l_1+l_2}+\mathscr{E}'''_{h_1+2h_2,\,h_2+k_1,\,h_2+l_1}$$
$$+\mathscr{E}'''_{h_1+k_2,\,k_1+2k_2,\,k_2+l_1}+\mathscr{E}'''_{h_1,\,k_1+k_2+\bar{l}_2,\,\bar{k}_2+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{l}_2,\,k_1,\,\bar{h}_2+l_1+l_2})$$
$$-\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_2}(3\mathscr{E}'''_{h_2,\,\bar{h}_1+k_1+k_2+l_1,\,\bar{h}_1+k_1+l_1+l_2}$$
$$+3\mathscr{E}'''_{h_1+h_2+\bar{k}_1+l_1,\,k_2,\,h_1+\bar{k}_1+l_1+l_2}$$
$$+3\mathscr{E}'''_{h_1+h_2+k_1+\bar{l}_1,\,h_1+k_1+k_2+\bar{l}_1,\,l_2}$$
$$+\mathscr{E}'''_{h_2+l_1,\,\bar{h}_1+k_1+k_2,\,\bar{h}_1+k_1+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{k}_1,\,k_2+l_1,\,h_1+\bar{k}_1+l_1+l_2}+\mathscr{E}'''_{h_2+l_1,\,k_2+l_1,\,2l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{k}_1,\,\bar{h}_1+k_1+k_2,\,l_2}+\mathscr{E}'''_{h_1+h_2+\bar{k}_1+l_1,\,h_1+k_2,\,\bar{k}_1+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{l}_1,\,h_1+k_1+k_2+\bar{l}_1,\,k_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+k_1+\bar{l}_1,\,h_1+k_2+\bar{l}_1,\,h_1+l_2}$$
$$+\mathscr{E}'''_{h_2+k_1,\,\bar{h}_1+k_1+k_2+l_1,\,\bar{h}_1+l_1+l_2}+\mathscr{E}'''_{2h_1+h_2,\,h_1+k_2,\,h_1+l_2}$$
$$+\mathscr{E}'''_{h_2+k_1,\,2k_1+k_2,\,k_1+l_2}+\mathscr{E}'''_{h_2,\,k_1+k_2+\bar{l}_1,\,\bar{k}_1+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{l}_1,\,k_2,\,\bar{h}_1+l_1+l_2})$$
$$-\frac{\sigma_8^{1/2}}{\sigma_4}\mathscr{E}'_{\mathbf{h}_1+\mathbf{h}_2}(3\mathscr{E}'''_{h_1+h_2,\,h_1+k_2+\bar{l}_1,\,h_1+\bar{k}_1+l_2}$$
$$+3\mathscr{E}'''_{h_2+k_1+\bar{l}_1,\,k_1+k_2,\,\bar{h}_1+k_1+l_2}+3\mathscr{E}'''_{h_2+\bar{k}_1+l_1,\,\bar{h}_1+k_2+l_1,\,l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{l}_2,\,h_2+k_1,\,h_2+\bar{k}_2+l_1}+\mathscr{E}'''_{h_1+k_2,\,k_1+k_2+\bar{l}_2,\,\bar{h}_2+k_2+l_1}$$
$$+\mathscr{E}'''_{h_1+h_2+\bar{l}_2,\,k_1+k_2+l_2,\,l_1+\bar{l}_2}+\mathscr{E}'''_{h_1+k_2,\,h_2+k_1,\,l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+k_2+\bar{l}_2,\,\bar{h}_2+k_1+k_2,\,k_2+l_1}+\mathscr{E}'''_{h_1+l_2,\,\bar{h}_2+k_1+l_2,\,\bar{k}_2+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+\bar{k}_2+l_2,\,k_1+l_2,\,\bar{h}_2+l_1+l_2}+\mathscr{E}'''_{h_1+h_2+\bar{k}_2,\,h_2+k_1+\bar{l}_2,\,h_2+l_1}$$
$$+\mathscr{E}'''_{h_1+\bar{k}_2,\,\bar{h}_2+k_1+k_2,\,\bar{h}_2+l_1+l_2}+\mathscr{E}'''_{h_1+h_2+\bar{l}_2,\,k_1+\bar{k}_2,\,\bar{k}_2+l_1+l_2}$$
$$+\mathscr{E}'''_{h_1+h_2,\,k_1+l_2,\,k_2+l_1}+\mathscr{E}'''_{h_1+l_2,\,k_1+k_2,\,h_2+l_1})\,, \tag{6·17}$$

and

$$\underline{{}_{13}R_{3,\,0}}={}_{11}R_{3,\,0}\,. \tag{6·18}$$

Next we define (where $C_n(t)$ is replaced by C_n):

$$\underline{{}_{9}R'_{2,\,0}}=-\frac{\sigma_8^{1/2}}{\sigma_4}(\mathscr{E}'''_{2h00}+\mathscr{E}'''_{02k0}+\mathscr{E}'''_{002l})$$
$$-\frac{8\sigma_6}{C_1\sigma_2\sigma_4}(2C_1-C_2)+\varrho_9\,, \tag{6·19}$$

where,

$$\varrho_9=\frac{4\sigma_8^{1/2}}{C_1\sigma_2\sigma_4^{1/2}}(2C_1-C_2)\mathscr{E}'_{\mathbf{h}}\mathscr{E}'''_{\mathbf{h}}$$
$$-\frac{\sigma_4}{2C_1\sigma_2^2}(8C_1-6C_2+C_3)\mathscr{E}'^2_{\mathbf{h}}+\frac{\sigma_4}{16C_1^2\sigma_2^2}$$
$$\times((2C_1-C_2)^2+4C_1(8C_1-6C_2+C_3))+\ldots\,, \tag{6·20}$$

$$\underline{{}_{10}R'_{2,\,0}}=\varrho_2+\varrho_{10}\,, \tag{6·21}$$

where,

$$\varrho_{10}=\frac{28\sigma_8^{1/2}}{C_1\sigma_2\sigma_4^{1/2}}(2C_1-C_2)\mathscr{E}'_{\mathbf{h}}\mathscr{E}'''_{\mathbf{h}}$$
$$-\frac{7\sigma_4}{2C_1\sigma_2^2}(8C_1-6C_2+C_3)\mathscr{E}'^2_{\mathbf{h}}$$
$$-\frac{98\sigma_6}{C_1\sigma_2\sigma_4}(2C_1-C_2)+\frac{7\sigma_4}{16\sigma_2^2}$$
$$\times((2C_1-C_2)^2+4C_1(8C_1-6C_2+C_3))+\ldots\,, \tag{6·22}$$

$$\underline{{}_{11}R'_{2,\,0}}=-\frac{\sigma_8^{1/2}}{\sigma_4}(\mathscr{E}'''_{0,\,\bar{h}+k+l,\,\bar{h}+k+l}+\mathscr{E}'''_{h+\bar{k}+l,\,0,\,h+\bar{k}+l}$$
$$+\mathscr{E}'''_{h+k+\bar{l},\,h+k+\bar{l},\,0})-\frac{8\sigma_6}{C_1\sigma_2\sigma_4}(2C_1-C_2)+\varrho_9\,, \tag{6·23}$$

$$\underline{{}_{12}R'_{2,\,0}}=\varrho_4+\varrho_{10}\,, \tag{6·24}$$

$$\underline{{}_{13}R'_{2,\,0}}=-\frac{\sigma_8^{1/2}}{\sigma_4}(\mathscr{E}'''_{0,\,\bar{h}+k+l,\,\bar{h}+k+l}+\mathscr{E}'''_{h+\bar{k}+l,\,0,\,h+\bar{k}+l}$$
$$+\mathscr{E}'''_{h+k+\bar{l},\,h+k+\bar{l},\,0})-\frac{4\sigma_6}{C_1\sigma_2\sigma_4}(2C_1-C_2)+\varrho_9\,, \tag{6·25}$$

$$\underline{{}_9R'_{3,0}}=\frac{\sigma_4^{1/2}}{8C_1\sigma_2}(2C_1-C_2)(\mathscr{E}'^2_{\mathbf{h}_1}+\mathscr{E}'^2_{\mathbf{h}_2}+\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_5\,, \tag{6·26}$$

$$\underline{{}_{10}R'_{3,0}}=\frac{7\sigma_4^{1/2}}{8C_1\sigma_2}(2C_1-C_2)(\mathscr{E}'^2_{\mathbf{h}_1}+\mathscr{E}'^2_{\mathbf{h}_2}+\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_6\,, \tag{6·27}$$

$$\underline{{}_{11}R'_{3,0}}=\frac{\sigma_4^{1/2}}{8C_1\sigma_2}(2C_1-C_2)(\mathscr{E}'^2_{\mathbf{h}_1}+\mathscr{E}'^2_{\mathbf{h}_2}+\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_7\,, \tag{6·28}$$

$$\underline{{}_{12}R'_{3,0}}=\frac{7\sigma_4^{1/2}}{8C_1\sigma_2}(2C_1-C_2)(\mathscr{E}'^2_{\mathbf{h}_1}+\mathscr{E}'^2_{\mathbf{h}_2}+\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_8\,, \tag{6·29}$$

and

$$\underline{{}_{13}R'_{3,0}}=\underline{{}_{11}R'_{3,0}}\,. \tag{6·30}$$

In order to summarize the relations among the correction terms for the various space groups in type $3P_2$, it is convenient to make the identification,

$$R\equiv R^{(0)}\,, \tag{6·31}$$

$$R'\equiv R^{(1)}\,. \tag{6·32}$$

Thus, for space groups, $R\bar{3}$, $R\bar{3}m$ and $R\bar{3}c$,

$$R^{(j)}_{i,0}={}_1R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·33}$$

For space groups, $Pm3$, $Pn3$ and $Pa3$,

$$R^{(j)}_{i,0}={}_1R^{(j)}_{i,0}+{}_9R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·34}$$

For space groups, $Pm3m$, $Pn3n$, $Pm3n$ and $Pn3m$,

$$R^{(j)}_{i,0}={}_1R^{(j)}_{i,0}+{}_{10}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·35}$$

For space groups, $Fm3$ and $Fd3$,

$$R^{(j)}_{i,0}={}_1R^{(j)}_{i,0}+{}_{11}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·36}$$

For space groups, $Fm3m$, $Fm3c$, $Fd3m$ and $Fd3c$,

$$R^{(j)}_{i,0}={}_1R^{(j)}_{i,0}+{}_{12}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·37}$$

Finally, for space groups $Fmmm$ and $Fddd$,

$$R^{(j)}_{i,0}={}_1R^{(j)}_{i,0}+{}_{13}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·38}$$

Note that $\underline{{}_1R_{2,0}}$, $\underline{{}_1R_{3,0}}$, $\underline{{}_1R'_{2,0}}$ and $\underline{{}_1R'_{3,0}}$ are defined in 1*P* (1959).

The remainder terms in the basic formulas are especially simple for the special case $p=q=r=2$. For this case, the formulas reduce to those obtainable by the algebraic methods proposed by us (1957).

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The Crystal Structure of K_5Hg_7

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K_5Hg_7 has an orthorhombic unit cell with $a=10{\cdot}06$, $b=19{\cdot}45$, $c=8{\cdot}34$ Å, $Z=4$, space group, *Pbcm*. The intensity data were obtained from Weissenberg and precession photographs of single crystals. The structure was determined by Patterson and electron-density methods and refined by the least-squares method. The K_5Hg_7 structure results from that of KHg_2 (a distorted AlB_2 structure) by replacing one-eighth of the Hg atoms by potassium atoms.

Introduction

The crystal structure of K_5Hg_7 is the fourth of a series of potassium amalgams whose structures have been determined. KHg_{11} is isotructural with $BaHg_{11}$, whose structure was reported by Peyronel (1952). The structures of KHg_2 and KHg were reported by Duwell & Baenziger (1955).

Due to the stoichiometry of KHg_{11} the mercury atoms form a three-dimensional net which encompasses the potassium atoms. In the KHg and KHg_2 structures, although not required by stoichiometry, the Hg atoms tend to group together. In KHg, the Hg atoms form nearly planar square groups of four which are strung together in chains by bonds between corners of the square groups. In KHg_2 the mercury atoms form puckered hexagonal layer nets—a distortion of the $NaHg_2(AlB_2)$ ideal structure type. The K_5Hg_7 structure reported below results from the KHg_2 structure by replacing every eighth mercury atom by a potassium atom in a regular way.

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