dimensions of the I_3^- ion by a re-investigation of the crystal structure of CsI_3.

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Sign Determination in Crystal Structure Analysis*

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Selection rules (applying to centrosymmetrical crystals only, but for all types of Bravais lattice) are given in tabular form for the correct choice of three X-ray reflexions to which arbitrary signs may be applied as the initial step towards sign determination by statistical methods.

Certain direct methods of crystal structure determination depend upon the fact that if the signs of a very few strong reflexions from a centrosymmetrical crystal are known, others can be deduced, at least with a considerable degree of probability.

Zachariasen (1952) has pointed out that 'since the origin may be shifted from one inversion center to another, it is possible to choose the signs of three structure factors at will', and by choosing a positive sign for the reflexions (201), (35$\bar{3}$) and (017) he succeeded in determining the signs of 198 of the largest Fourier coefficients for monoclinic metaboric acid.

This method can be applied with confidence only if a judicious choice of the original three reflexions is made.‡ (These methods are not, of course, always successful even when correctly applied.) The choice must be such that relative to the eight centres of symmetry in any unit cell (not related by a lattice translation) the signs of the three reflexions will be respectively as shown in Table 1. For certain combinations of reflexions not all these eight possibilities are covered, and in that case the validity of choosing arbitrary signs for three planes is destroyed.

Table 1. *Possible combinations of signs of three reflexions*

$h_1k_1l_1$	+	+	+	+	−	−	−	−
$h_2k_2l_2$	+	+	−	−	−	−	+	+
$h_3k_3l_3$	+	−	+	−	−	+	−	+

The selection rules depend on the nature of the lattice; apart from this they are independent of system, class or space group, although space-group extinctions may further restrict the choice by reducing to zero intensity some reflexions in axial zones that would otherwise have been allowed.

In this paper we have attempted to show, in a non-mathematical way, the reasons for the selection rules, and to tabulate them so that they can be used directly.

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* All derivations and proofs are omitted from this paper to economize space. The complete paper, in which the rules for axial zones and the list of space groups are also given explicitly, is available in duplicated form on application to the authors.

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‡ This was first pointed out to us, in principle, in a private conversation with Dr H. Lipson.

Table 2. *Coordinates of the eight centres of symmetry (not related by lattice translations) for the various types of lattice*

$P(R)$	0, 0, 0	$\frac{1}{2}$, 0, 0	0, $\frac{1}{2}$, 0	0, 0, $\frac{1}{2}$	$\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$	0, $\frac{1}{2}$, $\frac{1}{2}$	$\frac{1}{2}$, 0, $\frac{1}{2}$	$\frac{1}{2}$, $\frac{1}{2}$, 0
C (cf. A, B)	0, 0, 0	$\frac{1}{2}$, 0, 0	$\frac{1}{2}$, 0, $\frac{1}{2}$	0, 0, $\frac{1}{2}$	$\frac{1}{4}$, $\frac{1}{4}$, 0	$\frac{3}{4}$, $\frac{1}{4}$, 0	$\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{2}$	$\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$
I	0, 0, 0	$\frac{1}{2}$, 0, 0	0, $\frac{1}{2}$, 0	0, 0, $\frac{1}{2}$	$\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$	$\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{4}$	$\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{4}$	$\frac{1}{4}$, $\frac{1}{4}$, $\frac{3}{4}$
F	0, 0, 0	$\frac{1}{2}$, 0, 0	$\frac{1}{4}$, $\frac{1}{4}$, 0	$\frac{3}{4}$, $\frac{1}{4}$, 0	$\frac{1}{4}$, 0, $\frac{1}{4}$	$\frac{3}{4}$, 0, $\frac{1}{4}$	0, $\frac{1}{4}$, $\frac{1}{4}$	$\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{4}$

Table 3. *Rules governing the selection of three reflexions, $h_1k_1l_1$, $h_2k_2l_2$, $h_3k_3l_3$, to which arbitrary signs (say +, +, +) may be assigned as the initial step towards sign determination for a number of intense reflexions by probability methods*

	$P(R)$	C (cf. A, B)	I	F
I	$2n,2n,2n$ excluded	$2n,2n,2n$ excluded unless $h+k = 4n+2$	$2n,2n,2n$ excluded unless $h+k+l = 4n+2$	$2n,2n,2n$ excluded if h, k, l are *all* $4n$ or *all* $4n+2$
	[e.g. 204 forbidden]	[e.g. 204 allowed; 220 forbidden]	[e.g. 204 allowed; 220 forbidden]	[e.g. 220 allowed; 222, 400 forbidden]
II	No two of the three selected *hkl* reflexions may be of the same type			
	[e.g. 203 and $22\bar{1}$ allowed separately, but forbidden together because both are of the type $2n,2n,2n+1$]	Note: $h+k = 4n$* and $h+k = 4n+2$ are different types [e.g. 203 and $4\bar{2}1$ forbidden together; 203 and $22\bar{1}$ allowed separately and together]	Note: $h+k+l = 4n$* and $h+k+l = 4n+2$ are different types [e.g. $21\bar{1}$ and 231 forbidden together; 211 and 231 allowed]	The $(h+k)$, $(k+l)$ and $(l+h)$* values must not be the *same* mixture of $4n$ and $4n+2$ in any two of the three planes chosen [e.g. $11\bar{1}$ and $3\bar{1}1$ forbidden together; 111 (where $k+l = 2$) and $3\bar{1}1$ (where $k+l = 0$) allowed]
III	Σh $(= h_1+h_2+h_3)$, Σk, Σl must not *all* be even	Σh, Σk, Σl must not all be even unless $\Sigma(h+k) = 4n+2$*	Σh, Σk, Σl must not all be even unless $\Sigma(h+k+l) = 4n+2$*	Σh, Σk, Σl must not all be even unless at least one of $\Sigma(h+k)$, $\Sigma(k+l)$ and $\Sigma(l+h) = 4n+2$*
	[e.g. 013, $12\bar{4}$ and 135 allowed separately but forbidden together]	[e.g. $1\bar{1}3$, 115 and 201 forbidden together ($\Sigma(h+k) = 4$); $1\bar{1}3$, 115 and 221 allowed ($\Sigma(h+k) = 6$)]	[e.g. 213, 121 and $1\bar{1}2$ forbidden together ($\Sigma(h+k+l) = 12$); 213, 121 and $1\bar{1}4$ allowed ($\Sigma(h+k+l) = 14$)]	[e.g. 115, $3\bar{1}1$ and 002 forbidden together; 115, $3\bar{1}1$ and 202 allowed because $\Sigma(h+k) = 6$]

* *All* additions are algebraic.

Selection rules, expressed in a different and more mathematical form, are given for the centrosymmetrical space groups by Hauptman & Karle (1953). In their treatment a primitive triplet is chosen in all types of lattice. We have retained the normal choice of crystallographic axes.

For a centrosymmetrical structure the general structure factor $F(hkl) = 2\Sigma\Sigma f(hkl) \cos 2\pi(hx+ky+lz)$ can be regarded as due to scattering from a single atom of scattering power $|F(hkl)|$, placed at a centre of symmetry. For the various types of lattice the positions of the eight centres of symmetry not related by lattice translations are as shown in Table 2. If for any lattice the corresponding eight values of x, y, z for these centres of symmetry are substituted in $\cos 2\pi(hx+ky+lz)$ and are found to give *all* the eight possible sign combinations (Table 1) for the three initial reflexions *hkl*, then it follows that *one* of the centres of symmetry must be the origin for any arbitrary combination of signs.

The selection rules are enumerated in Table 3. Rule I applies to any one of the reflexions taken separately, rule II to any two, rule III to the three reflexions considered together. As in the *International Tables*, $2n$ means *any* even, and $2n+1$ *any* odd number. The examples given should make this clear.

These rules, in modified form, apply also to the selection of two reflexions to be given arbitrary signs in any one axial zone. The selection of three reflexions in two axial zones (h_1k_10, $0k_20$, $0k_3l_3$, say) so as to ensure that the two Fourier projections are referred to the same origin may be made in a limited number of space groups only. It can be shown that the above selection rules eliminate all combinations of three reflexions of the type H, H', and $H+H'$, such as would be involved in probability relationships (Cochran, 1952).

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