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**A reinforced non-negativity criterion.** By TOR LÖFGREN, *Institute of Chemistry, University of Uppsala, Uppsala, Sweden*

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The non-negativity of the expected  $\rho$  function is its only property that is used to advantage in deriving the Harker & Kasper (1948) or the Karle & Hauptman (1950) inequalities. The resulting relations prove weak for space groups with no translational symmetry (Löfgren, 1960). A natural extension of the non-negativity criterion is to claim that every  $\rho$  interval,  $(\rho, \rho + d\rho)$ , is represented by the correct volume,  $A(\rho) \cdot d\rho$ , in the unit cell (Löfgren, 1961). General  $A$  criteria are evidently more powerful than the non-negativity criterion ( $A(\rho) = 0$  for  $\rho < 0$ ), but at the same time, the relations are far more complicated than, say, the Harker-Kasper inequalities. There is sometimes an alternative way of introducing conditions additional to those of non-negativity without, however, essentially changing the practical tractability.

The traditional principle of non-negativity states (or *should* state; compare footnote below) that there exist  $gF(\mathbf{h})$ 's (for the prefix  $g$ , see Löfgren, 1960) such that  $|gF(\mathbf{h})|$  is equal to, say, the 'unitarized' observed structure amplitudes,  $|U(\mathbf{h})|$ , in so far as these are experimentally available, and such that, everywhere,  $\rho(\mathbf{r}) \geq 0$  for correct phases. Fig. 1 is an arbitrary one-dimensional case, the full curve giving  $\rho$  for some incorrect phase angles, the full curve giving  $\rho$  for some incorrect phase angles. The diagonally shaded surface is a 'forbidden' area.

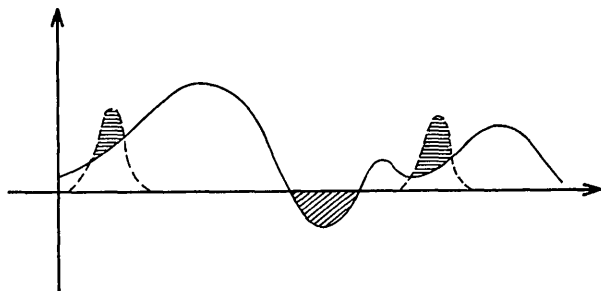


Fig. 1. The full curve gives  $\rho$  for incorrect phase angles, the dashed curves give the contribution to the correct  $\rho$  from atoms with known positions. Shaded areas are forbidden according to the reinforced non-negativity criterion.

For correct phases,  $\rho(\mathbf{r})$  is approximately equal to the model

$$\sum_n g\rho(n)(\mathbf{r} - \mathbf{r}(n)).$$

Now, if it is assumed that some atom or atoms have known positions, additional forbidden areas—horizontally shaded in Fig. 1—might appear. Our reinforced criterion is then, that for correct phases,

$$\rho(\mathbf{r}) - \sum'_n g\rho(n)(\mathbf{r} - \mathbf{r}(n)) \geq 0, \quad (1)$$

the prime indicating summation for (any choice among) the atoms with known positions. Expressed in terms of, say, Harker-Kasper inequalities, the  $U(\mathbf{h})$ 's may be replaced by the 'unitarized'

$$V(\mathbf{h}) = \frac{U(\mathbf{h}) - \sum'_n g f(n) \cdot \exp [2\pi i \mathbf{h} \cdot \mathbf{r}(n)]}{1 - \sum'_n g f(n)}, \quad (2)$$

where  $g f(n)$ , corresponding to  $g\rho(n)(\mathbf{r})$ , is that part of the total electron content of the cell attributed to the  $n$ th atom.\*

Any inequality can be written

$$C(U(\mathbf{h}'), U(\mathbf{h}''), \dots, U(\mathbf{h}^{(v)})) \geq 0, \quad (3)$$

where  $C$  is some function of the  $U$ 's (or  $V$ 's) considered. For a centrosymmetric case,  $C(x', x'', \dots, x^{(v)}) = 0$  is a surface in a  $v$ -dimensional space dividing the space in one forbidden part and one allowed part containing the origin. (An example is found in the paper by Klug (1958), Fig. 4.) If we set  $x' = \pm |U(\mathbf{h}')|$ ,  $x'' = \pm |U(\mathbf{h}'')|$ , etc., we get  $2^v$  points, of which certain may fall outside the surface  $C = 0$ . If so, certain sign combinations are excluded. The symmetry of the  $2^v$  points and of the surface  $C = 0$  is generally such that the result can be expressed as a sign relation. The setting (cf. (2))

$$x' = (\pm |U(\mathbf{h}')| - \sum'_n g f(n) \cdot \exp [2\pi i \mathbf{h}' \cdot \mathbf{r}(n)]) / (1 - \sum'_n g f(n)),$$

etc., implies that each of the  $2^v$  vectors

$$(\pm |U(\mathbf{h}')|, \pm |U(\mathbf{h}'')|, \dots)$$

is increased by the same vector

$$\begin{aligned} &(- \sum'_n g f(n) \cdot \exp [2\pi i \mathbf{h}' \cdot \mathbf{r}(n)], \\ &\quad - \sum'_n g f(n) \cdot \exp [2\pi i \mathbf{h}'' \cdot \mathbf{r}(n)], \dots), \end{aligned}$$

and the resulting vectors increased in length by the factor

$$(1 - \sum'_n g f(n))^{-1}.$$

The original symmetry is thereby destroyed and the result is not generally expressible as a sign relation but as excluded sign combinations. The exclusion of certain sign combinations is evidently a less valuable result, especially for large  $v$ 's, than are sign relations. However, definite signs are more likely results for  $V$ 's than for  $U$ 's.

With respect to statistical results and common experience, it is of interest to notice that anyone of the points  $(\pm U(\mathbf{h}'), \pm U(\mathbf{h}''), \dots)$  lying close to but inside the surface  $C = 0$ , has a high probability of leading to a corresponding point  $(\pm V(\mathbf{h}'), \pm V(\mathbf{h}''), \dots)$  lying outside this surface. For instance, if there exists any group of atoms in the cell giving very small contributions to the  $U$ 's considered, the vector  $(\pm V(\mathbf{h}'), \pm V(\mathbf{h}''), \dots)$  is simply the vector  $(\pm U(\mathbf{h}'), \pm U(\mathbf{h}''), \dots)$  increased in length by the factor

$$(1 - \sum''_n g f(n))^{-1},$$

where  $\sum''$  includes the group of atoms in question.

Some constructed examples have been worked through

\* Such constant  $g f(n)(\mathbf{h})$ 's are generally used to define a 'point atom'; evidently, they do not define a convergent function of  $\mathbf{r}$ . Starting with, say, a Gaussian atom (Gaussian transform) a non-negative 'point atom' can be defined, however, by a limiting process, satisfying the definition of  $g f(n)(\mathbf{h})$ , given in the text, for any finite part of the reciprocal space.

in order to make an empirical assessment of the relative powers of the traditional and reinforced inequalities. It was then found that the reinforced criterion can give definite signs and several exclusions of sign combinations, even when the traditional inequalities gave no information.

If the known atoms are in positions having the same symmetry as the rest of the structure, no particular type of inequality is expected to be especially affected. In the case where the atoms with known positions define a higher symmetry than the rest, certain inequalities will be reinforced to a greater extent than others. However, since it would be natural to calculate

$$\sum_n' af(n) \cdot \exp [2\pi i \mathbf{h} \cdot \mathbf{r}(n)]$$

for all  $\mathbf{h}$ 's simultaneously, there is little point in discussing particular situations in detail. It is evident that a sum,

$$\sum_n' af(n) \cdot \exp [2\pi i \mathbf{h} \cdot \mathbf{r}(n)],$$

that is large, whatever the cause might be, is particularly capable of increasing the power of an inequality.

It seems specially valuable to consider the reinforcement proposed here in the case in which some atomic positions are determined by symmetry, because

$$\sum_n' af(n) \cdot \exp [2\pi i \mathbf{h} \cdot \mathbf{r}(n)]$$

is then exactly known, and  $V$  very easily found from  $U$ .

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### Cell parameters and space groups of potassium, rubidium, and cesium acid chloromaleates.\*

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The cell parameters and space groups of the potassium, rubidium, and cesium acid chloromaleates

( $\text{HOOC} \cdot \text{CCl} : \text{CH} \cdot \text{COOM}$ , where  $M = \text{K, Rb, or Cs}$ )

grown from aqueous solution were determined. Preliminary values of the cell constants as well as symmetry information were found from photographs prepared with  $\text{Mo } K\alpha$  radiation on the precession camera. Powder diffraction data taken with a Debye-Scherrer camera and  $\text{Cr } K\alpha$  radiation were used in subsequent least-squares refinements of the cell dimensions. Densities were measured pycnometrically; the supporting liquid was  $n$ -decane.

Potassium acid chloromaleate was found to be orthorhombic. Precession camera pictures indexed as  $h0l$ ,  $h1l$ ,  $h2l$ ,  $0kl$ ,  $1kl$ ,  $2kl$ , and  $hk0$  display the following systematic absences: none among reflections  $hkl$ ;  $hk0$  reflections present only if  $h+k=2n$ ;  $h0l$ , only if  $l=2n$ ; and  $0kl$ , only if  $k=2n$ . These absences indicate the space group

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$Pbcn$ . A previous report (Yardley, 1925) gave cell dimensions in good agreement with those of this study, but a different space group ( $Pmcn$ , referred to the present axis orientation). The disagreement rests on two weak reflections which are absent on our photographs.

The space group of the two isomorphous monoclinic salts rubidium and cesium acid chloromaleate was not uniquely determined. On the precession camera pictures  $hk0$ ,  $hk1$ ,  $hk2$ ,  $0kl$ ,  $1kl$ , and  $2kl$ , the only systematic absences noted were those for which  $h+k+l=2n+1$ . Of the three space groups  $Im$ ,  $I2$  and  $I2/m$ , which are consistent with these absences, the last is considered unlikely because it requires that two chloromaleate ions lie in mirror planes in the approximately five by eight Ångström face of the cell.

The findings of this study are summarized in Table 1. In the monoclinic cases, the more usual  $C$ -centered cell is included, but the body-centered cell with  $\beta$  close to  $90^\circ$  is retained for convenience. The observed interplanar spacings, corrected for error due to absorption in the specimen (Klug & Alexander, 1954), are compared with the calculated values in Tables 2, 3, and 4. Indexing of

Table 1. *Crystallographic data for potassium, rubidium, and cesium acid chloromaleates*

	Potassium	Rubidium		Cesium	
		Body-centered indexing	$C$ -centered indexing	Body-centered indexing	$C$ -centered indexing
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
$a$	$15.815 \pm 0.015 \text{ \AA}$	$8.112 \pm 0.003 \text{ \AA}$	$9.61 \text{ \AA}$	$8.352 \pm 0.007 \text{ \AA}$	$9.87 \text{ \AA}$
$b$	$10.928 \pm 0.006$	$16.638 \pm 0.011$	$16.64$	$17.325 \pm 0.014$	$17.33$
$c$	$7.707 \pm 0.005$	$5.090 \pm 0.003$	$5.09$	$5.152 \pm 0.004$	$5.15$
$\beta$	—	$90^\circ 28' \pm 4'$	$122^\circ 26'$	$90^\circ 45' \pm 5'$	$122^\circ 12'$
Space group	$Pbcn$	$Im$ or $I2$	$Cm$ or $C2$	$Im$ or $I2$	$Cm$ or $C2$
Molecules/cell	8		4		4
Calculated density	$1.881 \text{ g.cm.}^{-3}$		$2.272 \text{ g.cm.}^{-3}$		$2.516 \text{ g.cm.}^{-3}$
Observed density	1.868		2.246		2.515

The errors listed are least-squares standard deviations.