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Linear Structure-Factor Inequalities and their Application to the Structure Determination of Tetragonal Ethylenediamine Sulphate.

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We have derived new linear structure-factor inequalities for crystals with centres of symmetry. We have also introduced the concept of arbitrariness in the systematic applications of the inequality methods. We have applied our linear inequalities to the U_{hk0}'s and U_{h0l}'s of tetragonal ethylenediamine sulphate (of hitherto unknown structure), and have determined almost all the signs of important structure factors within a few hours. With these signs, we have synthesized electron-density projections from which we have assigned approximate atomic positions to all atoms except hydrogen.

Introduction

Using the inequality of Cauchy,

$$|\sum_i a_i b_i|^2 \leqq \{\sum_i |a_i|^2\}\{\sum_i |b_i|^2\}, \quad (1)$$

Harker & Kasper (1947, 1948) and then Gillis (1948*a*) have obtained relations between the magnitudes of some structure factors and the signs or phases of others. These relations, the so-called Harker–Kasper inequalities, have since proved to be very useful for the determination of crystal structures. Examples of applications have been reported in the papers by Gillis (1948*b*)* on monoclinic oxalic acid dihydrate $(COOH)_2.2H_2O$, by Kasper, Lucht & Harker (1950) on orthorhombic decaborane $B_{10}H_{14}$, and by Burbank (1951) on α-selenium, Se_8.

However, in the practical application of the Harker–Kasper method one has to use inequalities containing quadratic terms of structure factors, and this causes the computation, as well as a preliminary inspection, to be rather involved. Thus it would be more useful if inequalities containing only linear terms could be found. The present paper deals with this problem, first limiting it to crystals with centres of symmetry. The case of crystals without centres of symmetry will be dealt with later.

The so-called unitary structure factor, U_{hkl}, which we shall use hereafter, may be given the following form for crystals with centres of symmetry:

$$U_{hkl} = \frac{F_{hkl}}{F_{000}\cdot\hat{f}} = \sum_i n_i \cos 2\pi(hx_i+ky_i+lz_i), \quad (2)$$

where F_{hkl} is the ordinary structure factor, $F_{000} = \sum_i Z_i$ = total number of electrons in the unit cell, $\hat{f}$ = the unitary atomic scattering factor (in the sense of Harker–Kasper), and $n_i = Z_i/\sum_i Z_i$, Z_i being the number of electrons in the ith atom. This formula is based on the assumption of a similar charge distibution in all atoms. The unitary structure factors have the following property:

$$|U_{hkl}| \leqq 1{\cdot}00, \quad (3)$$

$$U_{000} = 1{\cdot}00. \quad (3')$$

Derivation of linear inequalities

It is well known that, in general, if a_i and b_i are real,

$$a_i^2+b_i^2 \geqq 2|a_i b_i|, \quad (4)$$

and, as

$$\sum_i |a_i b_i| \geqq |\sum_i a_i b_i|,$$

one obtains

$$\sum_i n_i a_i^2 + \sum_i n_i b_i^2 \geqq 2|\sum_i n_i a_i b_i|, \quad (5)$$

with positive n_i's.

In the first place, if we put in (5),

$$\left.\begin{aligned} a_i &= \cos 2\pi(hx_i+ky_i+lz_i), \\ b_i &= 1/m, \end{aligned}\right\} \quad (6)$$

where h, k and l are integers and, for the sake of convenience, $m \geqq 0$, we obtain

$$\sum_i n_i + \sum_i n_i \cos 2\pi(2hx_i+2ky_i+2lz_i) + \sum_i n_i \frac{2}{m^2} \geqq \frac{4}{m}|\sum_i n_i \cos 2\pi(hx_i+ky_i+lz_i)|, \quad (7)$$

which further becomes on combining with (2), and since $\Sigma n_i = 1$,

$$2+m^2+m^2U_{2h,2k,2l} \geqq 4m|U_{hkl}|. \quad (8)$$

Putting for example $m = 1$, 2 and $\frac{1}{2}$ in (8), we obtain respectively,

$$3+U_{2h,2k,2l} \geqq 4|U_{hkl}|, \quad (8a)$$

* Cf. some remarks by us (Okaya & Nitta, 1952).

$$3+2U_{2h,2k,2l} \geqq 4|U_{hkl}| , \qquad (8b)$$

and

$$2+U_{2h,2k,2l} \geqq 2\sqrt{2}.|U_{hkl}| . \qquad (8c)$$

Obviously, the relation (8*b*) is more effective than the other two for narrowing inequality relations.

In the second place, if we put in (5),

$$\left.\begin{aligned} a_i &= \cos 2\pi(px_i+qy_i+rz_i) , \\ b_i &= m \cos 2\pi(p'x_i+q'y_i+r'z_i) , \ m \geqq 0 , \end{aligned}\right\} \qquad (9)$$

we obtain

$$\begin{aligned} &\sum_i n_i[1+m^2+\cos 2\pi(2px_i+2qy_i+2rz_i) \\ &\quad +m^2 \cos 2\pi(2p'x_i+2q'y_i+2r'z_i)] \\ &\geqq 2m|\sum_i n_i [\cos 2\pi\{(p+p')x_i+(q+q')y_i+(r+r')z_i\} \\ &\quad +\cos 2\pi\{(p-p')x_i+(q-q')y_i+(r-r')z_i\}]| . \end{aligned} \qquad (10)$$

On replacing $p+p'$, $q+q'$, $r+r'$; $p-p'$, $q-q'$, $r-r'$ by h, k, l; h', k', l' respectively, and on assuming that the latter are integers, we obtain from (10)

$$1+m^2+U_{h+h',k+k',l+l'}+m^2U_{h-h',k-k',l-l'} \geqq 2m|U_{hkl}+U_{h'k'l'}| . \qquad (11)$$

Similarly, we obtain another relation:

$$1+m^2+m^2U_{h+h',k+k',l+l'}+U_{h-h',k-k',l-l'} \geqq 2m|U_{hkl}+U_{h'k'l'}| . \qquad (12)$$

Putting $m = 1, 2$ and $\sqrt{2}$ in (11) and (12) we get respectively,

$$2+U_{h+h',k+k',l+l'}+U_{h-h',k-k',l-l'} \geqq 2|U_{hkl}+U_{h'k'l'}| , \qquad (11a)$$

$$5+U_{h+h',k+k',l+l'}+4U_{h-h',k-k',l-l'} \geqq 4|U_{hkl}+U_{h'k'l'}| , \qquad (11b)$$

$$5+4U_{h+h',k+k',l+l'}+U_{h-h',k-k',l-l'} \geqq 4|U_{hkl}+U_{h'k'l'}| , \qquad (12b)$$

$$3+U_{h+h',k+k',l+l'}+2U_{h-h',k-k',l-l'} \geqq 2\sqrt{2}|U_{hkl}+U_{h'k'l'}| , \qquad (11c)$$

and

$$3+2U_{h+h',k+k',l+l'}+U_{h-h',k-k',l-l'} \geqq 2\sqrt{2}|U_{hkl}+U_{h'k'l'}| . \qquad (12c)$$

The relation (11*a*) can also be obtained from (12) by putting $m = 1$, and might be numbered as (12*a*).

In the third place, if we put in (5),

$$\left.\begin{aligned} a_i &= \sin 2\pi(px_i+qy_i+rz_i) , \\ b_i &= m \sin 2\pi(p'x_i+q'y_i+r'z_i) , \ m \geqq 0 , \end{aligned}\right\} \qquad (13)$$

we obtain

$$\begin{aligned} &\sum_i n_i[1+m^2-\cos 2\pi(2px_i+2qy_i+2rz_i) \\ &\quad -m^2 \cos 2\pi(2p'x_i+2q'y_i+2r'z_i)] \\ &\geqq 2m|\sum_i n_i \cos 2\pi\{(p+p')x_i+(q+q')y_i+(r+r')z_i\} \\ &\quad -\cos 2\pi\{(p-p')x_i+(q-q')y_i+(r-r')z_i\}]| , \end{aligned} \qquad (14)$$

and, by the same substitution as above,

$$1+m^2-U_{h+h',k+k',l+l'}-m^2U_{h-h',k-k',l-l'} \geqq 2m|U_{hkl}-U_{h'k'l'}| . \qquad (15)$$

Similarly, we have

$$1+m^2-m^2U_{h+h',k+k',l+l'}-U_{h-h',k-k',l-l'} \geqq 2m|U_{hkl}-U_{h'k'l'}| . \qquad (16)$$

Putting $m = 1$, 2 and $\sqrt{2}$ in (15) and (16), we get, respectively,

$$2-U_{h+h',k+k',l+l'}-U_{h-h',k-k',l-l'} \geqq 2|U_{hkl}-U_{h'k'l'}| , \qquad (15a)$$

$$5-U_{h+h',k+k',l+l'}-4U_{h-h',k-k',l-l'} \geqq 4|U_{hkl}-U_{h'k'l'}| , \qquad (15b)$$

$$5-4U_{h+h',k+k',l+l'}-U_{h-h',k-k',l-l'} \geqq 4|U_{hkl}-U_{h'k'l'}| , \qquad (16b)$$

$$3-U_{h+h',k+k',l+l'}-2U_{h-h',k-k',l-l'} \geqq 2\sqrt{2}|U_{hkl}-U_{h'k'l'}| , \qquad (15c)$$

and

$$3-2U_{h+h',k+k',l+l'}-U_{h-h',k-k',l-l'} \geqq 2\sqrt{2}|U_{hkl}-U_{h'k'l'}| . \qquad (16c)$$

Lastly, by putting in (5)

$$\left.\begin{aligned} a_i &= p \cos 2\pi(hx_i+ky_i+lz_i) \\ &\quad +q \cos 2\pi(h'x_i+k'y_i+l'z_i) , \\ b &= r , \quad r \geqq 0 , \end{aligned}\right\} \qquad (17)$$

we obtain, omitting the intermediate derivations:

$$\begin{aligned} &p^2+q^2+2r^2+p^2U_{2h,2k,2l}+q^2U_{2h',2k',2l'}+2pq(U_{h+h',k+k',l+} \\ &\quad +U_{h-h',k-k',l-l'}) \geqq 4r|pU_{hkl}+qU_{h'k'l'}| . \end{aligned} \qquad (18)$$

All these formulae are also valid for non-integral values of h, k and l.

Discussion of derived inequalities

The above inequalities (8), (11), (12), (15), (16) and (18) have been derived for crystals with centres of symmetry. However, in practical applications we use inequalities between structure factors of the form (*hkl*) with one index zero. In such cases we need not confine ourselves to crystals with three-dimensional centres of symmetry, but can make use of the inequalities if a principal projection, (*hk*0), (0*kl*) or (*h*0*l*), has centro-symmetry.

As we have already pointed out in a short note (Okaya & Nitta, 1952), it is essential to ascertain at the beginning of a phase determination how many arbitrary sign parameters will remain undetermined owing to the possibility of choosing the origin at different centres of symmetry. In the case of projections having additional centres of symmetry this multiplicity of the answer will be increased.

By comparing the inequalities (11) and (12), or (15) and (16), we see that either one of the inequality pairs may be chosen with an adequate m value, so as to make the relation more strongly restrictive.

It is easily verified mathematically that our inequality relations are numerically less restrictive on phase relations than those of Harker–Kasper. However, in actual application, this apparent disadvantage is of minor significance, as we have checked in the cases of phase determination applied to U_{h0l}'s of monoclinic oxalic acid dihydrate (Gillis, 1948*b*), U_{hk0}'s of tetragonal pentaerythritol (Watanabé & Nitta, 1938) and to U_{hk0}'s of orthorhombic hydrazonium sulphate (Nitta, Sakurai & Tomiie, 1951), where the phases of structure factors were already known. The great convenience of our inequalities comes from their linear form; this simplifies computation to the point that by simple inspection adequate structure factors can be picked out between which the inequalities operate successfully. This advantage is quite important when one works on unknown structures by means of the inequality method. Moreover, by introducing an appropriate weighting coefficient m, we can largely eliminate errors due to more or less inaccurate U_{hkl} values or to those not observed.

When a crystal possesses further symmetry elements, besides centres of symmetry, forms of inequalities can be derived other than those given above. However, such introduction of various formulae, valid for special cases, only causes formal complications of minor practical value. Therefore, they will not be further considered. We can always use the original inequalities; the other symmetry elements then give additional equality relations between structure factors. Further remarks will be given in the following paragraphs.

Before applying our inequalities to the case of the unknown structure of tetragonal ethylenediamine sulphate, we summarize the most useful inequalities in Table 1.

Table 1. *Most useful inequalities*

$$3+2U_{2h,2k,2l} \geqq 4|U_{hkl}|\,, \qquad (8b)$$

$$2+U_{h+h',k+k',l+l'}+U_{h-h',k-k',l-l'} \geqq 2|U_{hkl}+U_{h'k'l'}|\,, \qquad (11a)$$

$$2-U_{h+h',k+k',l+l'}-U_{h-h',k-k',l-l'} \geqq 2|U_{hkl}-U_{h'k'l'}|\,, \qquad (15a)$$

$$5+U_{h+h',k+k',l+l'}+4U_{h-h',k-k',l-l'} \geqq 4|U_{hkl}+U_{h'k'l'}|\,, \qquad (11b)$$

$$5-U_{h+h',k+k',l+l'}-4U_{h-h',k-k',l-l'} \geqq 4|U_{hkl}-U_{h'k'l'}|\,, \qquad (15b)$$

$$5+4U_{h+h',k+k',l+l'}+U_{h-h',k-k',l-l'} \geqq 4|U_{hkl}+U_{h'k'l'}|\,, \qquad (12b)$$

$$5-4U_{h+h',k+k',l+l'}-U_{h-h',k-k',l-l'} \geqq 4|U_{hkl}-U_{h'k'l'}|\,. \qquad (16b)$$

We have also solved the structure of monoclinic aspirin by means of these inequalities; this will be published later.

Application to tetragonal ethylenediamine sulphate, $(CH_2NH_2)_2.H_2SO_4$

In order to show how simply our inequalities are applied, the case of ethylenediamine sulphate will be given here. The experimental data have been kindly supplied by K. Sakurai and Y. Tomiie, to whom our thanks are due; they will report the detailed analysis of this crystal in the near future. The tetragonal unit cell, containing eight formula units, has dimensions

$$a = 8{\cdot}45 \quad \text{and} \quad c = 17{\cdot}99 \text{ Å}\,.$$

The space group, D_4^4–$C4_122_1$, follows from the systematic absences: (hkl) for $h+k \neq 2n$, $(hh0)$ for $h \neq 2n$ and $(00l)$ for $l \neq 4n$. There is no centre of symmetry in the three-dimensional sense, but the projections onto the $(x\,y)$, $(y\,z)$ and $(x\,z)$ planes have centres of symmetry, so that our method is applicable. The axes could be so chosen that the unit cell becomes simple tetragonal containing four molecules, but we shall adhere to the choice of Sakurai & Tomiie.

Tables 2 and 3 list the values of the $|U_{hk0}|$'s and $|U_{h0l}|$'s, as calculated by Sakurai & Tomiie using the method of Wilson (1949), with a temperature factor with $B = 1{\cdot}0$ Å^2. From the consideration of the symmetry elements of the space group, it is seen that the following relations between the U_{hk0}'s hold (origin on a twofold axis):

$$U_{hk0} = U_{\bar{h}k0} = U_{k\bar{h}0} = U_{\bar{k}\bar{h}0} \text{ for } h \text{ and } k \text{ both even,} \qquad (19)$$

and

$$U_{hk0} = U_{\bar{h}k0} = -U_{k\bar{h}0} = -U_{\bar{k}\bar{h}0} \text{ for } h \text{ and } k \text{ both odd,} \qquad (20)$$

and that there is one arbitrary parameter connected to the U_{hk0}'s with h and k odd. Further, between the U_{h0l}'s the following relations exist:

$$U_{h0l} = U_{h0\bar{l}} \text{ for } l = \text{even,} \qquad (21)$$

$$U_{h0l} = -U_{h0\bar{l}} \text{ for } l = \text{odd,} \qquad (22)$$

Table 2. $|U_{hk0}|$'s, *ethylenediamine sulphate*

$k \backslash h$	0	1	2	3	4	5	6	7	8	9	10
0	1·00	(0·00)	0·08	(0·00)	0·17	(0·00)	0·00	(0·00)	0·69	(0·00)	0·00
1	(0·00)	(0·00)	(0·00)	0·10	(0·00)	0·00	(0·00)	0·37	(0·00)	0·32	(0·00)
2	0·08	(0·00)	0·30	(0·00)	0·09	(0·00)	0·45	(0·00)	0·00	(0·00)	0·40
3	(0·00)	0·10	(0·00)	(0·00)	(0·00)	0·24	(0·00)	0·00	(0·00)	0·39	(0·00)
4	0·17	(0·00)	0·09	(0·00)	0·84	(0·00)	0·09	(0·00)	0·00	(0·00)	0·00
5	(0·00)	0·00	(0·00)	0·24	(0·00)	(0·00)	(0·00)	0·32	(0·00)	0·00	
6	0·00	(0·00)	0·45	(0·00)	0·09	(0·00)	0·60	(0·00)	0·13		
7	(0·00)	0·37	(0·00)	0·00	(0·00)	0·32	(0·00)	(0·00)			
8	0·69	(0·00)	0·00	(0·00)	0·00	(0·00)	0·13				
9	(0·00)	0·32	(0·00)	0·39	(0·00)	0·00					
10	0·00	(0·00)	0·40	(0·00)	0·00						

(0·00) means absences by extinction rules.

Table 3. $|U_{h0l}|$'s, *ethylenediamine sulphate*

l\h	0	2	4	6	8	10
0	1·00	0·08	0·17	0·00	0·69	0·00
1	(0·00)	0·20	0·08	0·03	0·41	0·67
2	(0·00)	0·29	0·08	0·34	0·00	0·37
3	(0·00)	0·00	0·10	0·27	0·24	0·23
4	0·22	0·00	0·24	0·12	0·49	0·00
5	(0·00)	0·26	0·27	0·13	0·17	0·35
6	(0·00)	0·16	0·13	0·53	0·15	0·26
7	(0·00)	0·10	0·24	0·39	0·00	
8	0·33	0·11	0·47	0·22	0·33	
9	(0·00)	0·26	0·28	0·28	0·00	
10	(0·00)	0·07	0·00	0·39	0·00	
11	(0·00)	0·15	0·30	0·00	0·00	
12	0·00	0·00	0·40	0·00	0·00	
13	(0·00)	0·00	0·00	0·00	0·00	
14	(0·00)	0·13	0·00	0·00	0·31	
15	(0·00)	0·00	0·00	0·14	0·22	
16	0·52	0·00	0·37	0·00		
17	(0·00)	0·00	0·00	0·00		
18	(0·00)	0·57	0·00	0·29		
19	(0·00)	0·00	0·00	0·34		
20	0·37	0·00	0·58			
21	(0·00)	0·00	0·23			
22	(0·00)	0·52				

(0·00) means absences by extinction rules.

and also there are two arbitrary parameters; one connected to the U_{h0l}'s with l = odd, and the other to those with $h = 2\times$odd. The above four relations would have taken a slightly different form if we had chosen the simple unit cell.

Procedure for determining the phases of the U_{hk0}'s

By (11a)

$$2+U_{080}+U_{800} \geqq 2|U_{440}+U_{4\bar{4}0}| , \qquad (T\,1)$$

where $U_{800} = U_{080}$ and $U_{440} = U_{4\bar{4}0}$ by (19).

Calling S_{hk0} the sign of U_{hk0}, and using the values of Table 2, (T 1) becomes

$$2+2\times 0{\cdot}69S_{080} \geqq 2|0{\cdot}84+0{\cdot}84| ,$$

or

$$1+0{\cdot}69S_{080} \geqq 1{\cdot}68 ,$$

and we have obviously

$$S_{080} = +1 . \qquad (R\,1)$$

By (12b)

$$5+4U_{440}+U_{8\bar{8}0} \geqq 4|U_{6\bar{2}0}+U_{2\bar{6}0}| , \qquad (T\,2)$$

with $U_{6\bar{2}0} = U_{2\bar{6}0}$ by (19), and thus

$$5+4\times 0{\cdot}84S_{440}+U_{8\bar{8}0} \geqq 4|0{\cdot}45+0{\cdot}45| .$$

Here, although $U_{8\bar{8}0}$ is not observed, we can easily say

$$S_{440} = +1 , \qquad (R\,2)$$

because generally $|U_{8\bar{8}0}| \leqq 1{\cdot}00$.

By (11b) and (15b) we have

$$5\pm U_{10,\bar{2},0}\pm 4U_{620} \geqq 4|U_{800}\pm U_{2\bar{2}0}| , \qquad (T\,3)$$

from which, using (R 1),

$$5\pm 0{\cdot}40S_{10,2,0}\pm 4\times 0{\cdot}45S_{620} \geqq 4|0{\cdot}69\pm 0{\cdot}30S_{220}| .$$

If we take $S_{220} = +1$ in the sum formula of (T 3), we have $S_{620} = +1$, whereas if $S_{220} = -1$ in the difference formula, we have $S_{620} = -1$, so we obtain

$$S_{620} = S_{220} = a , \qquad (R\,3)$$

a being used for the sake of later convenience.

On the other hand, by (12b) and (16b) we have

$$5\pm 4U_{10,\bar{2},0}\pm U_{620} \geqq 4|U_{800}\pm U_{2\bar{2}0}| , \qquad (T\,4)$$

and quite similarly we obtain

$$S_{10,2,0} = S_{220} = a . \qquad (R\,4)$$

Next, by (11a) and (15a),

$$2\pm U_{2,10,0}\pm U_{10,2,0} \geqq 2|U_{660}\pm U_{4\bar{4}0}| , \qquad (T\,5)$$

which becomes, using (R 2) and (R 4),

$$2\pm 2\times 0{\cdot}40a \geqq 2|0{\cdot}60S_{660}\pm 0{\cdot}84| .$$

In the sum formula, $a = +1$, if $S_{660} = +1$, and in the difference formula, $a = -1$, if $S_{660} = -1$. In the derivation of these conclusions some numerical contradictions arose; these can be attributed to errors in the U_{hk0}'s used, possibly, or at least partly, due to the use of the too small value $B = 1{\cdot}0$ Å^2 in the temperature factor. Thus we have

$$S_{660} = a . \qquad (R\,5)$$

By (11b) and (15b)

$$5\pm 4U_{570}\pm U_{13,\bar{1},0} \geqq 4|U_{930}\pm U_{4\bar{4}0}| , \qquad (T\,6)$$

which gives, using (R 2),

$$5\pm 4\times 0{\cdot}32S_{570}\pm U_{13\bar{1}0} \geqq 4|0{\cdot}39S_{930}\pm 0{\cdot}84| .$$

From this we obtain, as before,

$$S_{930} = S_{570} .$$

As we have already mentioned, there is an arbitrariness in choosing the signs of U_{hk0}'s with h and k odd, and we put accordingly

$$S_{930} = S_{570} = x , \qquad (R\,6)$$

where x is an arbitrary parameter.

By (11a) and (15a) we have

$$2\pm U_{660}\pm U_{2\bar{6}0} \geqq 2|U_{400}\pm U_{260}| , \qquad (T\,7)$$

which becomes, using (R 3) and (R 5),

$$2\pm 0{\cdot}60a\pm 0{\cdot}45a \geqq 2|0{\cdot}17S_{400}\pm 0{\cdot}45a| .$$

In the sum formula, if $S_{400} = a$, we have $a = +1$, and in the difference formula, if $S_{400} = -a$, we have $a = -1$. Thus

$$S_{400} = +1 . \qquad (R\,7)$$

By (15a) we have

Table 4. *The phases of U_{hk0}'s, as determined*

$k\backslash h$	0	1	2	3	4	5	6	7	8	9	10
0	+1·00	(0·00)	|0·08|	(0·00)	+0·17	(0·00)	0·00	(0·00)	+0·69	(0·00)	0·00
1	(0·00)	(0·00)	(0·00)	$-0·10x$	(0·00)	0·00	(0·00)	$-0·37x$	(0·00)	$+0·32x$	(0·00)
2	|0·08|	(0·00)	−0·30	(0·00)	|0·09|	(0·00)	−0·45	(0·00)	0·00	(0·00)	−0·40
3	(0·00)	$+0·10x$	(0·00)	(0·00)	(0·00)	$+0·24x$	(0·00)	0·00	(0·00)	$+0·39x$	(0·00)
4	+0·17	(0·00)	|0·09|	(0·00)	+0·84	(0·00)	|0·09|	(0·00)	0·00	(0·00)	0·00
5	(0·00)	0·00	(0·00)	$-0·24x$	(0·00)	(0·00)	(0·00)	$-0·32x$	(0·00)	0·00	
6	0·00	(0·00)	−0·45	(0·00)	|0·09|	(0·00)	−0·60	(0·00)	|0·13|		
7	(0·00)	$+0·37x$	(0·00)	0·00	(0·00)	$+0·32x$	(0·00)	(0·00)			
8	+0·69	(0·00)	0·00	(0·00)	0·00	(0·00)	|0·13|				
9	(0·00)	$-0·32x$	(0·00)	$-0·39x$	(0·00)	0·00					
10	0·00	(0·00)	−0·40	(0·00)	0·00						

(0·00) means absences by extinction rules.
$|U_{hk0}| \leqq 0·13$, which remain undetermined.
x arbitrarily assignable.

$$2-U_{10,\bar{2},0}-U_{440} \geqq 2|U_{710}-U_{3\bar{3}0}| , \qquad (T\,8)$$

which becomes, using (R 2) and (R 4) as well as the extinction rule,

$$2-0·40a-0·84 \geqq 2|0·37S_{710}-0| .$$

Although we obtain from this $a = +1$ and $a = -1$, the former can be regarded as improbable from the consideration of the nature of inequality relation as well as the uncertainty due to the inexact temperature factor. Thus we obtain

$$a = -1 . \qquad (R\,8)$$

Up to this stage we have determined the signs of all important structure factors U_{hk0}'s with h and k both even.

Next, by (11a) and (15a),

$$2\pm U_{570}\pm U_{310} \geqq 2|U_{130}\pm U_{440}| , \qquad (T\,9)$$

which becomes, using (R 2), (R 6) and (20),

$$2\pm 0·32x\mp 0·10S_{130} \geqq 2|0·10S_{130}\pm 0·84| ,$$

and hence

$$S_{130} = x . \qquad (R\,9)$$

By (11a) and (15a) we have

$$2\pm U_{1\bar{7}0}\pm U_{190} \geqq 2|U_{110}\pm U_{080}| , \qquad (T\,10)$$

which gives, using (R 1) and the extinction rule,

$$2\pm 0·37S_{170}\pm 0·32S_{190} \geqq 2|0\pm 0·69| .$$

As the sum and difference relations must hold simultaneously, we have

$$S_{170} = -S_{190} = bx , \qquad (R\,10)$$

where a factor b is introduced to adjust their relation to $S_{570} = x$.

By (11a) and (15a) we have

$$2\pm U_{710}\pm U_{\bar{1}90} \geqq 2|U_{350}\pm U_{440}| , \qquad (T\,11)$$

which becomes, using (R 2), (R 10) and (20),

$$2\pm(-0·37bx)\pm(-0·32bx) \geqq 2|0·25S_{350}\pm 0·84| ,$$

and hence, as above, we get

$$S_{350} = -bx . \qquad (R\,11)$$

Up to now we have obtained the signs of all important structure factors U_{hk0}'s with h and k both even as well as h and k both odd, except for a condition concerning the value of b. For its determination, we also use (11a) and (15a), from which we have

$$2\pm U_{950}\pm U_{5\bar{7}0} \geqq 2|U_{7\bar{1}0}\pm U_{260}| , \qquad (T\,12)$$

which becomes, using (R 3), (R 6), (R 8) and (R 10),

$$2\pm 0·00\pm 0·32x \geqq 2|-0·37bx\pm(-0·45)| ,$$

$$2\pm 0·32x \geqq 2|0·37bx\pm 0·45| .$$

Here we get two conditions,

$$bx = \pm x ,$$

from which we choose, by a similar consideration as used in the case of (R 8),

$$bx = +x ;$$

that is

$$b = +1 . \qquad (R\,12)$$

The structure factors of which the signs have so far been determined are the U_{hk0}'s with absolute values greater than 0·13, and these are given in Table 4.

Procedure for determining the phases of the U_{h0l}'s

For U_{h0l}'s the method is the same as for the U_{hk0}'s, except for the use of the equality relations (21) and (22). For brevity only some illustrative examples of the tests used will be given, together with the corresponding T and R series of formulae. As will be seen in these formulae, we also used some results already obtained in the preceding paragraph, such as the signs of U_{400} and U_{800}.

$$5 + U_{800} + 4U_{6,0,16} \geqq 4|U_{40\bar{8}} + U_{408}| , \qquad (T\,13)$$

$$2 \pm U_{804} \pm U_{80\bar{4}} \geqq 2|U_{800} \pm U_{004}| , \qquad (T\,14)$$

$$2 \pm U_{308} \pm U_{80\bar{8}} \geqq 2|U_{800} \pm U_{008}| , \qquad (T\,15)$$

Table 5. *The phases of U_{h0l}'s, as determined*

l \ h	0	2	4	6	8	10
0	+1·00	|0·08|	+0·17	0·00	+0·69	0·00
1	(0·00)	+0·20yz	|0·08|	|0·03|	−0·41z	+0·67yz
2	(0·00)	+0·29y	|0·08|	+0·34y	0·00	+0·37y
3	(0·00)	0·00	|0·10|	|0·27|	|0·24|	+0·23yz
4	+0·22	0·00	+0·24	|0·12|	+0·49	0·00
5	(0·00)	+0·26yz	−0·27z	|0·13|	|0·17|	+0·35yz
6	(0·00)	+0·16y	|0·13|	+0·53y	|0·15|	|0·26|
7	(0·00)	|0·10|	+0·24z	−0·39yz	0·00	
8	+0·33	|0·11|	+0·47	|0·22|	+0·33	
9	(0·00)	+0·26yz	−0·28z	+0·28yz	0·00	
10	(0·00)	+0·07y	0·00	+0·39y	0·00	
11	(0·00)	|0·15|	+0·30z	0·00	0·00	
12	0·00	0·00	+0·40	0·00	0·00	
13	(0·00)	0·00	0·00	0·00	0·00	
14	(0·00)	|0·13|	0·00	0·00	|0·31|	
15	(0·00)	0·00	0·00	|0·14|	|0·22|	
16	+0·52	0·00	+0·37	0·00		
17	(0·00)	0·00	0·00	0·00		
18	(0·00)	+0·57y	0·00	+0·29y		
19	(0·00)	0·00	0·00	−0·34yz		
20	+0·37	0·00	+0·58			
21	(0·00)	0·00	−0·23z			
22	(0·00)	+0·52y				

(0·00) means absences by extinction rules.
$|U_{h0l}|$ which remain undetermined.

$$2 + U_{4,0,16} + U_{4,0,\bar{16}} \geqq 2|U_{400} + U_{0,0,16}|\,, \quad (T\,16)$$

$$2 - U_{400} - U_{4,0,16} \geqq 2|U_{408} - U_{008}\,|\,, \quad (T\,17)$$

$$2 \pm U_{606} \pm U_{2,0,10} \geqq 2|U_{408} \pm U_{20\bar{2}}\,|\,, \quad (T\,18)$$

$$2 \pm U_{10,0,1} \pm U_{\bar{6}01} \geqq 2|U_{201} \pm U_{800}\,|\,, \quad (T\,19)$$

$$5 \pm U_{4,0,\overline{12}} \pm 4U_{4,0,20} \geqq 4|U_{404} \pm U_{0,0,16}|\,, \quad (T\,20)$$

$$5 \pm U_{14,0,21} \pm 4U_{6,0,\overline{19}} \geqq 4|U_{4,0,20} \pm U_{10,0,1}|\,, \quad (T\,21)$$

$$5 \pm 4U_{10,0,1} \pm U_{\bar{2},0,\overline{11}} \geqq 4|U_{40\bar{5}} \pm U_{606}\,|\,, \quad (T\,22)$$

$$5 \pm 4U_{10,0,\bar{1}} \pm U_{\bar{2},0,\overline{13}} \geqq 4|U_{40\bar{7}} \pm U_{606}\,|\,, \quad (T\,23)$$

$$5 \pm 4U_{10,0,\bar{1}} \pm U_{609} \geqq 4|U_{804} \pm U_{20\bar{5}}\,|\,, \quad (T\,24)$$

$$2 \pm U_{10,0,1} \pm U_{607} \geqq 2|U_{804} \pm U_{20\bar{3}}\,|\,, \quad (T\,25)$$

$$5 \pm 4U_{10,0,\bar{1}} \pm U_{2,0,15} \geqq 4|U_{607} \pm U_{40\bar{8}}\,|\,, \quad (T\,26)$$

$$5 \pm 4U_{10,0,1} \pm U_{2,0,17} \geqq 4|U_{609} \pm U_{40\bar{8}}\,|\,, \quad (T\,27)$$

$$5 \pm U_{10,0,2} \pm 4U_{2,0,18} \geqq 4|U_{6,0,10} \pm U_{40\bar{8}}\,|\,, \quad (T\,28)$$

$$2 \pm U_{6,0,14} \pm U_{602} \geqq 2|U_{808} \pm U_{206}\,|\,, \quad (T\,29)$$

$$2 \pm U_{4,0,20} \pm U_{404} \geqq 2|U_{4,0,12} \pm U_{008}\,|\,, \quad (T\,30)$$

$$5 \pm 4U_{10,0,5} \pm U_{\bar{6}05} \geqq 4|U_{205} \pm U_{800}\,|\,, \quad (T\,31)$$

$$2 \pm U_{2,0,21} \pm U_{\bar{10},0,1} \geqq 2|U_{4,0,11} \pm U_{6,0,10}|\,, \quad (T\,32)$$

$$2 \pm U_{10,0,1} \pm U_{2,0,\bar{9}} \geqq 2|U_{40\bar{9}} \pm U_{6,0,10}|\,, \quad (T\,33)$$

$$5 \pm U_{6,0,22} \pm 4U_{6,0,\overline{10}} \geqq 4|U_{606} \pm U_{0,0,16}|\,. \quad (T\,34)$$

The results are:

$$S_{0,0,16} = +1\,, \quad (R\,13)$$

$$S_{804} = S_{004} = a'\,, \quad (R\,14)$$

$$S_{808} = S_{008} = b'\,, \quad (R\,15)$$

$$S_{4,0,16} = +1\,, \quad (R\,16)$$

$$S_{408} = S_{008} = b'\,, \quad (R\,17)$$

$$S_{606} = b'S_{202} = b'y\,, \quad (R\,18)^*$$

$$S_{201} = S_{10,0,1} = yz\,, \quad (R\,19)\dagger$$

$$S_{4,0,20} = S_{404} = c'\,, \quad (R\,20)$$

$$S_{6,0,19} = -c'yz\,, \quad (R\,21)$$

$$S_{405} = -b'y^2z = -b'z\,, \quad (R\,22)$$

$$S_{407} = b'y^2z = b'z\,, \quad (R\,23)$$

$$S_{205} = a'yz\,, \quad (R\,24)$$

$$S_{607} = -yz\,, \quad (R\,25)$$

$$b' = +1\,, \quad (R\,26)$$

$$S_{609} = yz\,, \quad (R\,27)$$

$$S_{6,0,10} = S_{2,0,18} = d'y\,, \quad (R\,28)$$

$$S_{602} = y\,, \quad (R\,29)$$

$$S_{4,0,12} = c'\,, \quad (R\,30)$$

$$S_{10,0,5} = a'yz\,, \quad (R\,31)$$

$$S_{4,0,11} = d'y^2z = d'z\,, \quad (R\,32)$$

* y is an arbitrary parameter owing to an arbitrariness connected to the U_{h0l}'s with $h = 2\times$odd.

† z is a further arbitrary parameter owing to an arbitrariness connected to the U_{h0l}'s with $l =$ odd, and the product yz is connected to the U_{h0l}'s with $h = 2\times$odd and $l =$ odd.

$$S_{409} = -d'y^2z = -d'z\,, \qquad (R\ 33)$$

$$d' = +1\,. \qquad (R\ 34)\S$$

Using these relations, we obtain the signs of U_{h0l}'s in terms of $a', b', c', \ldots, y$ and z, the last two being the arbitrary parameters already mentioned. On fixing the values $a', b', \ldots$ by using appropriate relations, we come to the final results shown in Table 5.

Construction of electron-density maps

Following the procedures described in the preceding paragraphs, we have obtained all the signs of U_{hk0}'s with absolute values greater than 0·13 within an hour, and those of important U_{h0l}'s with absolute values greater than 0·17 within five hours. With their signs, after putting $x = +1$, $y = -1$ and $z = -1$ for the three arbitrary sign parameters, and neglecting all the smaller structure factors, we synthesized electron-density projections upon the $(x\,y)$ and $(x\,z)$ planes. These projections (Figs. 1 and 2) are seen to be

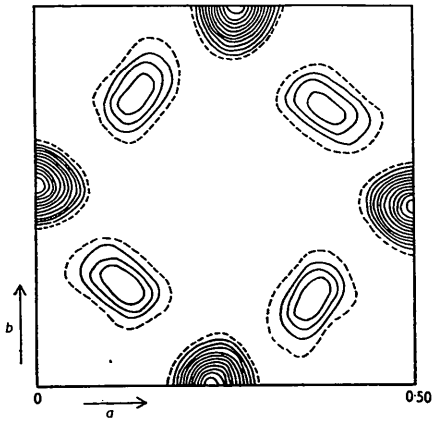

Fig. 1. Projection of electron density upon $(x\,y)$ plane, using the signs determined by the linear inequality method only. The arbitrary parameter x is assigned as $+1$. The contour lines are drawn on an arbitrary scale.

already pretty good, and enable us to locate all the atoms except hydrogen in approximate positions and thence to proceed to more exact atomic parameters. Inspection of the figures indicates that the ethylenediamine molecule or ethylenediaminium ion possesses an atomic configuration of the so-called gauche form. However, it is not the purpose of our present paper to go into the details of the crystal structure of this substance, which will be reported by Messrs K. Sakurai and Y. Tomiie in the near future. So far we have derived linear inequalities between structure factors of crystals with centres of symmetry and have illustrated the usefulness and simplicity of their

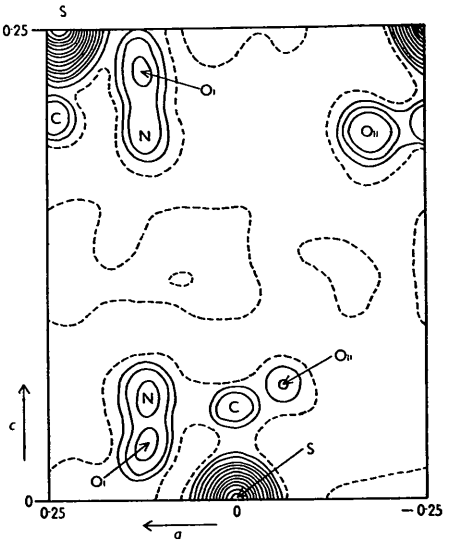

Fig. 2. Projection of electron density upon $(x\,z)$ plane, using the signs determined by the linear inequality method only. The arbitrary parameters y and z are both assigned as -1. The contour lines are drawn on an arbitrary scale.

practical application in structure determination. There remains another case of linear inequalities, valid for crystals without centre of symmetry, on which we intend to report soon.

We wish to express our thanks to Messrs K. Sakurai and Y. Tomiie for their kindness of putting their X-ray data for tetragonal ethylenediamine sulphate at our disposal and also for their valuable discussion of the present problem. The cost of this study was defrayed by the Ministry of Education.

§ (R 34) is deduced on the assumption that $|U_{6,0,22}| \leqq 0{\cdot}88$, although it lies beyond the observable index field.

References

BURBANK, R. D. (1951). *Acta Cryst.* **4**, 140.
GILLIS, J. (1948*a*). *Acta Cryst.* **1**, 76.
GILLIS, J. (1948*b*). *Acta Cryst.* **1**, 174.
HARKER, D. & KASPER, J. S. (1947). *J. Chem. Phys.* **15**, 882.
HARKER, D. & KASPER, J. S. (1948). *Acta Cryst.* **1**, 70.
KASPER, J. S., LUCHT, C. M. & HARKER, D. (1950). *Acta Cryst.* **3**, 436.
NITTA, I., SAKURAI, K. & TOMIIE, Y. (1951). *Acta Cryst.* **4**, 289.
OKAYA, Y. & NITTA, I. (1952). *Acta Cryst.* **5**, 291.
WATANABÉ, T. & NITTA, I. (1938). *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **34**, 1669.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.