Acta Cryst. (1961). **14**, 999

Location and shape of peak maxima in the Gaussian ellipsoid approximation.

By B. Dawson,
Division of Chemical Physics, C.S.I.R.O. Chemical Research Laboratories, Melbourne, Australia

(*Received* 30 *December* 1960)

For the location of Fourier peak maxima from the values of electron density ϱ calculated at grid points corresponding to d_1-, d_2-, d_3-fold division of the a-, b-, c-axes respectively, Shoemaker *et al.* (1950) approximate to the shape of a peak near its maximum by means of the Gaussian function

$$\varrho = \exp\,(p - \tfrac{1}{2}rx^2 - \tfrac{1}{2}sy^2 - \tfrac{1}{2}tz^2 + ux + vy + wz + lxy + mxz + nyz)\,. \quad (1)$$

The parameters p, r etc. are determined by least-squares from values of ϱ at points of a $3 \times 3 \times 3$ grid (Fig. 1) surrounding the maximum, the central point (ϱ_1) being taken as origin and the grid intervals along a, b and c being used as units of x, y and z. In the case of two-dimensional Fourier data, the Gaussian approximation is somewhat simpler (e.g. in $h0l$ and hKl generalized projections $s = v = l = n = 0$) and the determination of six parameters involves a 3×3 grid ($\varrho_1, \ldots, \varrho_9$, Fig. 1). Useful features of this method of locating maxima are that the lattice need not be orthogonal and the peaks may deviate considerably from spherical (or circular) shape, but these advantages appear initially to be offset by a complexity of data treatment which is greater than that involved in other methods of peak location (e.g. Ladell & Katz, 1954; Megaw, 1954). This complexity largely disappears, however, when a systematic procedure has been established for evaluating the p, r etc. from the various ϱ. This aspect of the method of Shoemaker *et al.* (1950) seems not to have been published so far and is therefore reported here.

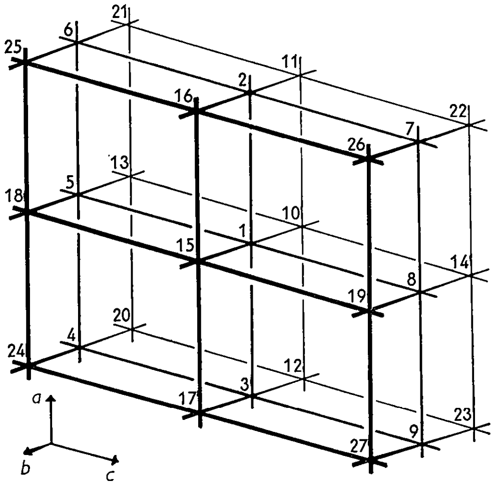

Fig. 1. The grid numbering to which Table 1 refers.

The least-squares parameter determinations yield expressions

$$p = 1/k_p \sum_i c_{i,p} \ln \varrho_i, \quad r = 1/k_r \sum_i c_{i,r} \ln \varrho_i \ \text{etc.}\,, \quad (2)$$

Table 1. *The values of k and c_i for the* 27-*point* (A), 19-*point* (B) *and* 9-*point* (C) *cases*

		$k \backslash c_i$ i =	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
p	A	27	7	4	4	1	4	1	1	4	1	4	1	1	1	1	4	1	1	1	1	-2	-2	-2	-2	-2	-2	-2	-2
	B	21	9	4	4	-1	4	-1	-1	4	-1	4	-1	-1	-1	-1	4	-1	-1	-1	-1								
	C	9	5	2	2	-1	2	-1	-1	2	-1																		
r	A	9	2	-1	-1	-1	2	-1	-1	2	-1	2	-1	-1	2	2	2	-1	-1	2	2	-1	-1	-1	-1	-1	-1	-1	-1
	B	21	10	-1	-1	-5	6	-5	-5	6	-5	6	-5	-5	2	2	6	-5	-5	2	2								
	C	3	2	-1	-1	-1	2	-1	-1	2	-1																		
s	A	9	2	2	2	2	2	2	2	2	2	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
	B	21	10	6	6	2	6	2	2	6	2	-1	-5	-5	-5	-5	-1	-5	-5	-5	-5								
t	A	9	2	2	2	-1	-1	-1	-1	-1	-1	2	2	2	-1	-1	2	2	2	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
	B	21	10	6	6	-5	-1	-5	-5	-1	-5	6	2	2	-5	-5	6	2	2	-5	-5								
	C	3	2	2	2	-1	-1	-1	-1	-1	-1																		
u	A	18	0	1	-1	-1	0	1	1	0	-1	0	1	-1	0	0	0	1	-1	0	0	-1	1	1	-1	-1	1	1	-1
	B	10	0	1	-1	-1	0	1	1	0	-1	0	1	-1	0	0	0	1	-1	0	0								
	C	6	0	1	-1	-1	0	1	1	0	-1																		
v	A	18	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	1	1	1	1	1	-1	-1	-1	-1	1	1	1	1
	B	10	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	1	1	1	1	1								
w	A	18	0	0	0	-1	-1	-1	1	1	1	0	0	0	-1	1	0	0	0	-1	1	-1	-1	1	1	-1	-1	1	1
	B	10	0	0	0	-1	-1	-1	1	1	1	0	0	0	-1	1	0	0	0	-1	1								
	C	6	0	0	0	-1	-1	-1	1	1	1																		
l	A	12	0	0	0	0	0	0	0	0	0	0	-1	1	0	0	0	1	-1	0	0	1	-1	1	1	-1	1	1	-1
	B	4	0	0	0	0	0	0	0	0	0	0	-1	1	0	0	0	1	-1	0	0								
m	A	12	0	0	0	1	0	-1	1	0	-1	0	0	0	0	0	0	0	0	0	0	1	-1	1	-1	1	-1	1	-1
	B	4	0	0	0	1	0	-1	1	0	-1	0	0	0	0	0	0	0	0	0	0								
	C	4	0	0	0	1	0	-1	1	0	-1																		
n	A	12	0	0	0	0	0	0	0	0	0	0	0	0	1	-1	0	0	0	-1	1	1	1	-1	-1	-1	-1	1	1
	B	4	0	0	0	0	0	0	0	0	0	0	0	0	1	-1	0	0	0	-1	1								

i.e. each parameter involves a single constant k and a series of constants c_i, one for each of the grid points used in the least-squares treatment. If all twenty-seven points are weighted equally then, *for the grid numbered as shown in Fig.* 1, the values of k and the c_i for each parameter are those in rows A, Table 1. If, however, the eight corner grid points are omitted in case their ϱ-values do not satisfy the Gaussian approximation adequately (Donohue & Trueblood, 1952), then equal weighting of the other nineteen gives the k and c_i in rows B, Table 1. For the two-dimensional instance noted earlier, equal weighting of the nine points now involved gives the results shown in rows C. The different parameter determinations are thus various simple linear combinations of the logarithms of the ϱ-values at the different grid points. A preliminary check on the adequacy of equation (1) near the peak centre is provided by the agreement between p and $\ln \varrho_1$.

Using the conditions $\partial\varrho/\partial x$ etc. $=0$ at the peak centre, the position of the centre with respect to grid point ϱ_1 is defined by the x-, y-, z-values satisfying the simultaneous equations

$$\begin{aligned} rx - ly - mz &= u \\ -\ lx + sy - nz &= v \\ -mx - ny + tz &= w\,. \end{aligned} \qquad (3)$$

With (X_1, Y_1, Z_1) the coordinates in Å of this grid point, the corresponding coordinates of the peak centre are therefore (X_1+xa/d_1, Y_1+yb/d_2, Z_1+zc/d_3). In the two-dimensional case in Table 1, the analogous equations for x and z reduce conveniently to

$$x=(ut+mw)/(rt-m^2),\quad z=(um+rw)/(rt-m^2)\,. \qquad (3a)$$

The central peak curvatures in e.Å^{-5} (or e.Å^{-4}) are

$$\begin{aligned} A_{hh} &= -r\varrho_0D_1^2, & A_{kk} &= -s\varrho_0D_2^2, & A_{ll} &= -t\varrho_0D_3^2 \\ A_{hk} &= l\varrho_0D_1D_2, & A_{hl} &= m\varrho_0D_1D_3, & A_{kl} &= n\varrho_0D_2D_3\,, \end{aligned} \qquad (4)$$

where $D_1=d_1/a$ etc. and ϱ_0 is the value of equation (1) for the x, y, z from equations (3).

In the 9-point case, experience here has shown that the time involved per peak, including tabulation of logarithms, is about 10–15 minutes on a desk calculator: a similar time for the 27-point case has been noted by Ibers (1956), presumably after the $\ln \varrho_i$ have been obtained. The simple nature of the various linear combinations of data shown in Table 1 is such that this method of peak location is readily adapted to a computer (Sparks *et al.*, 1956; Stephenson, 1960).

References

DONOHUE, J. & TRUEBLOOD, K. N. (1952). *Acta Cryst.* **5**, 419.
IBERS, J. A. (1956). *Acta Cryst.* **9**, 225.
LADELL, J. & KATZ, J. L. (1954). *Acta Cryst.* **7**, 460.
MEGAW, H. D. (1954). *Acta Cryst.* **7**, 771.
SHOEMAKER, D. P., DONOHUE, J., SCHOMAKER, V. & COREY, R. B. (1950). *J. Amer. Chem. Soc.* **72**, 2328.
SPARKS, R. A., PROSEN, R. J., KRUSE, F. H. & TRUEBLOOD, K. N. (1956). *Acta Cryst.* **9**, 350.
STEPHENSON, N. C. (1960). Private communication of independent work.

Acta Cryst. (1961). **14**, 1000

A refinement of the positional parameter in α-nitrogen.

By JERRY DONOHUE, *Department of Chemistry, University of Southern California, Los Angeles 7, California, U.S.A.*

(*Received* 20 *February* 1961)

Vegard (1929) assigned α-nitrogen to the space group $P2_13$–(T^4), and gave values for the two parameters which defined the positions of the eight nitrogen atoms in a unit cell with $a=5{\cdot}67$ Å (from kX.) at 20 °K. This structure, although the intramolecular N–N distance had the reasonable value of 1·07 Å, was odd in that the molecules lay in positions displaced in an unsymmetrical way from cubic close packing. Ruhemann (1932) did not observe either the (110) or the (310) reflections required by $P2_13$ and reported by Vegard, and pointed out that space group $Pa3$–(T_h^6) was also a possible one, but made no attempt to determine the single positional parameter of that space group; he found $a=5{\cdot}68\pm0{\cdot}02$ Å (from kX.) at 20 °K., in agreement with Vegard. Bolz *et al.* (1959), examined α-nitrogen condensed at 4·2 °K., found $a=5{\cdot}644\pm0{\cdot}005$ Å and a linear coefficient of expansion of 2×10^{-4} deg.$^{-1}$. (These values lead to $a=5{\cdot}662$ Å at 20 °K.) Not observing either (110) or (310), they concluded that the space group was $Pa3$, and provisionally reported the value $x=0{\cdot}054$ for the parameter. This value yields 1·056 Å for the N–N distance. They stated that their observed X-ray intensities, although in better agreement for the $Pa3$ structure than for the $P2_13$ structure, were not yet fully convincing, the difficulties arising, apparently, from structural faults due to too low an annealing temperature (13 °K.). Very recently, Hörl & Marton (1961) obtained electron diffraction data from thin films of nitrogen at 20 °K. They found $a=5{\cdot}661\pm0{\cdot}008$ Å, assumed space group $Pa3$ (the two crucial reflections were absent), but did not attempt an independent determination of the positional parameter. Instead, they adopted the value N–N of 1·094 Å (Herzberg, 1955), i.e., $x=0{\cdot}0558$, and found that a ±20% deviation from this internuclear distance 'would have shown very distinct differences even in visual estimates of the diffraction ring intensities.'

Although the internuclear distance of 1·094 Å is probably more reliable than one obtained by consideration of the rather limited powder diffraction data, there is, nevertheless, interest in refining the electron diffraction intensity data in order to find out what internuclear distance is obtained, and how it compares with that found in the free gas molecule.

The visually estimated intensities of the twenty lines tabulated by Hörl & Marton were treated by the method of least-squares, with simultaneous variation of the positional parameter, x, of $Pa3$ and the scale factor, k. The quantity minimized was