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

$$\begin{aligned} &A_{hh} = -r\varrho_0 D_1^2, \quad A_{kk} = -s\varrho_0 D_2^2, \quad A_{ll} = -t\varrho_0 D_3^2 \\ &A_{hk} = l\varrho_0 D_1 D_2, \quad A_{hl} = m\varrho_0 D_1 D_3, \quad A_{kl} = n\varrho_0 D_2 D_3\,, \end{aligned} \qquad (4)$$

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).

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A refinement of the positional parameter in α-nitrogen.

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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 $a = 5{\cdot}68 \pm 0{\cdot}02$ Å (from kX.) at 20 °K., in agreement with Vegard. Bolz *et al.* (1959), examined α-nitrogen condensed at 4·2 °K., found $a = 5{\cdot}644 \pm 0{\cdot}005$ 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 $a = 5{\cdot}661 \pm 0{\cdot}008$ 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

$$\sum_{hkl} w(kI_o - I_c)^2 ,$$

where $w = I_o^{-2}$. The formula

$$I = \text{const.}(Z - f)^2 (\Sigma h_i^2)^{-3} \Sigma p F^2$$

was used to compute the values of the I_c. A plot of I_o/I_c versus Σh_i^2 showed no indication of any trend, consequently no temperature factor was used. The values of $(Z - f)$ were deduced by comparison of the values of I_c listed by Hörl & Marton and those calculated with the above formula at $x = 0{\cdot}0558$ omitting the factor $(Z - f)^2$.

The results are: $x = 0{\cdot}0530$, $\sigma = 0{\cdot}0020$. The corresponding N–N distance is 1·04 Å, $\sigma = 0{\cdot}04$ Å, a result which does not differ significantly from the spectroscopic value. Thermal anisotropy, which cannot be determined with the data at hand, may account for part or all of the discrepancy, or, it may be that stacking faults, mentioned as a possibility by Hörl & Marton, give rise to intensity differences which lead to an error in the positional parameter. The observed and calculated intensities, for $x = 0{\cdot}0530$, are presented in Table 1. These data yield $R_I = 100\Sigma|I_o - I_c|/\Sigma I_o = 34\%$. The value of R_I for $x = 0{\cdot}0558$ is 39%. Fifteen of the reflections listed in Table 1 allow the calculation of $|F_o|$; for these

$$R = 100\Sigma||F_o - F_c||/\Sigma|F_o| = 17{\cdot}6\% .$$

It is interesting that the minimum value of R, 17·4%, occurs at $x = 0{\cdot}0545$.

In this structure each nitrogen atom has, in addition to the one intramolecular neighbor at 1·04 Å, six neighbors at 3·60 Å and six at 3·65 Å in adjacent molecules. The intermolecular distances (at 20 °K.) are much larger than the value 3·0 Å implied by the usual van der Waals radius (Pauling, 1960).

Table 1. *Diffraction data for α-nitrogen*

(hkl)*	I_o†	I_c	(hkl)	I_o	I_c
111	18,000	14,178	420	75	37
200	2,250	5,553	421	75	2
210	375	482	412		60
211	525	606	332	75	68
220	3,000	1,702	422	*a*	14
221	225	177	430	300	204
311	1,050	1,043	431	525	16
222	225	283	413		328
230	600	407	333	*a*	4
321	900	610	511		4
312		31	250	300	76
400	*a*	26	432		166
322	375	264	423		5
411	75	125	521	75	125
331	75	92	512		0

* Space group extinctions, to which Hörl & Martin assigned the value zero for both I_o and I_c, are omitted.

† Values of Hörl & Martin modified by a scale factor of 1·50.

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Unit cell and space group of cembrene.

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Cembrene, $C_{20}H_{32}$, is a diterpene found in the sap of the pine tree *Pinus albicaulis*. The crystals for this study were kindly supplied by Prof. W. G. Dauben of the University of California, Berkeley, and were used without further purification. The white crystals display a columnar habit. With precession photographs taken with copper K radiation filtered through nickel foil we have found the crystals to be orthorhombic with

$$a = 13{\cdot}8 \pm 0{\cdot}1,\ b = 21{\cdot}4 \pm 0{\cdot}2,\ c = 6{\cdot}24 \pm 0{\cdot}05 \text{ Å} .$$

On these photographs the even orders from the respective pinacoids were observed up to $h = 8$, $k = 14$, and $l = 4$, but no odd orders were observed. Reflections of all other types were present on the precession photographs of the $h0l$ and $0kl$ zones and on $hk0$ and hkl Weissenberg photographs. Hence the space group is probably D_2^4–$P2_12_12_1$. No test for a piezoelectric effect was made. The density measured by suspension of the crystals in a methanol–water gradient density column is $0{\cdot}98 \pm 0{\cdot}01$ g.cm.$^{-3}$, in excellent agreement with a density of 0·98 g.cm.$^{-3}$ calculated for four molecules in the unit cell.

This unit cell and space group determination was undertaken on the chance that such information might favor one of the several structures for cembrene proposed on the basis of chemical and physical evidence. This did not prove to be the case. Because of the size and complexity of the unit cell, no further work is contemplated on this structure.