In such a graph, R_∞ corresponds to a horizontal line plotted at $|\Delta F| = 0{\cdot}828\ \overline{|F|}$, where $\overline{|F|} = 0{\cdot}7979\overline{F^2}$. It is easy to see at which $\sin\theta$ value the average of $|\Delta F|$ approaches the R_∞ value, and also whether the scaling is reasonable. The next step is to draw a 'best' line through the significant low-order points, and then to find the 'half-way point', i.e., the value of $\sin\theta_h$ at which $\overline{|\Delta F|} = \frac{1}{2}\overline{|\Delta F|}_\infty$. At this point, $Q(\frac{1}{2}R_\infty) = 0{\cdot}485 = 2\pi H\sigma$, so that we obtain the desired σ from the relation

$$\sigma = \frac{0{\cdot}485}{2\pi H} = \frac{0{\cdot}485\lambda}{4\pi\sin\theta_h}\,. \qquad (31)$$

It should be realized that in the extreme case when $\sin\theta_h$ falls below the lowest $\sin\theta$ of the reflexion, only a lower limit of σ may be obtained.

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Interatomic Distances and Thermal Anisotropy in Sodium Nitrate and Calcite

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A re-determination of the parameters in calcite and sodium nitrate made by the use of all (Cu $K\alpha$) reflections due to oxygen scattering only, gives C–O = 1·294 Å and N–O = 1·218 Å, with estimated standard deviations of 0·004 Å in both. The parameter refinements were carried out by least squares, and by a Fourier method which isolated the oxygen atoms from the other atoms. Electron-density plots indicate considerable anisotropy in the motion of the anions, the oxygen atoms appearing distinctly reniform. The bond distances are compared with those in related compounds, and those predicted by simple valence-bond theory.

Introduction

The structure of calcite was one of the first to be determined by X-rays (Bragg, 1914). It is the type structure for a number of nitrates, carbonates, and borates, and is well suited for the determination of accurate interatomic distances because there is but one positional parameter. Approximate values of the parameter in calcite and sodium nitrate were obtained by Wyckoff (1920*a*, *b*); the first precise determinations of these quantities were those of Elliott (1937). In his work, Elliott made use of Laue data exclusively; seven pairs of reflections were used to determine the parameter in calcite, and three pairs in sodium nitrate. Although the intensities of these reflections were estimated very carefully by the use of an α-ray integrating photometer, it appeared desirable to redetermine the parameters with more extensive data, and to investigate the thermal anisotropy, because, as has been discovered recently in the case of benzene (Cox, Cruickshank & Smith, 1955), neglect of anisotropy of the sort which might be expected for the anions in these two crystals may have a significant effect on the values obtained for the interatomic distances. The parameter in sodium nitrate has also been determined by Tahvonen (1947), who used the trial-and-error method on powder data only.

Experimental

Approximately cylindrical crystals suitable for X-ray examination were obtained by cleavage of larger crystals. The sodium nitrate crystal was about 0·2 mm. in diameter ×5 mm., while that of calcite was about 0·08 mm. in diameter ×3 mm. Both crystals were dipped in liquid air to minimize extinction. The crystals were mounted with the axis of rotation along the long dimension, which was parallel to one of the edges of the cleavage rhombohedron. Multiple-film Weissenberg photographs were then taken with Cu$K\alpha$ radiation of the first four odd layer lines of the non-primitive (cleavage) rhombohedral unit cell. All the reflections on these layer lines are due only to scattering by the oxygen atoms. The intensities were estimated in the usual way with the aid of an intensity strip. Absorption was neglected. Because of the rotation axis chosen for Weissenberg photography, equivalent reflections were sometimes recorded on more than one layer line. In the case of calcite, for example, where twenty unique reflections were observed, four occurred on three different layer lines, and ten on two. Comparisons among these were used in setting all of the reflections on the same relative scale. The indices and coordinates used throughout refer to the hexagonal cell associated with the primitive rhombohedral cell. The atoms were placed in the following positions of space group D_{3d}^6–$R\bar{3}c$ (No. 167), as given in the *International Tables*:

Na or Ca in 6(*b*), N or C in 6(*a*), and O in 18(*e*).

The lattice constants used for calcite were those of Swanson & Fuyat (1953) who found

$$a = 4{\cdot}989\ \text{Å} \text{ and } c = 17{\cdot}062\ \text{Å}\,,$$

while those used for sodium nitrate were those of Swanson, Gilfrich & Cook (1956), who found

$$a = 5{\cdot}070\ \text{Å} \text{ and } c = 16{\cdot}829\ \text{Å}\,.$$

Refinement of parameters

Structure factors were first calculated with the parameters given by Elliott and the form-factor curve for oxygen of McWeeny (1951). Preliminary scale and average (isotropic) temperature factors were then estimated. The structure is such that the layers at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ are identical except for the orientation of the anions. Therefore, although the electron density expression for $\varrho(x, y, z)$ includes all F_{hkl}, the expression for $\varrho(x, y, \frac{1}{4}) - \varrho(x, y, \frac{3}{4})$ will include only those F_{hkl} to which oxygen terms alone contribute; these are the (hkl) with $l = 2n+1$. Since the reflections on the odd layer lines of the non-primitive rhombohedral cell include all reflections having l (hexagonal) odd and no others, the data collected furnish the terms required for the calculation of the electron-density difference above. Although the above expression yields a true electron-density difference, that term is obviously inappropriate for it, and we shall instead call it an isolation Fourier map, since the oxygen atoms are isolated from the others. Corresponding manipulation of the electron-density expression should be possible for many other structures, and could be useful for determining the parameters of light atoms in the presence of heavier ones by Fourier methods.

The isolation maps of both crystals indicated considerable anisotropy of the thermal motion of the oxygen atoms in the xy plane. This anisotropy apparently consists of a librational motion about the threefold axes of the anions, with the result that the atoms appeared to be distinctly reniform, as can be seen in Fig. 1, which shows the isolation map for calcite. In applying the corrections for the anisotropy to the calculated structure factors, however, no attempt was made to take the reniform shapes of the atoms into account; rather the elliptical treatment of Rollett & Davies (1955) was used. The Fourier parameters were corrected for back-shift in the usual way. The first isolation maps were made with calculated F values which included only an isotropic temperature factor. In these maps the oxygen atoms are circular. This result, together with the fact that subsequent maps made with calculated F values which included the anisotropic temperature factor resembled closely the maps made with the observed F values, shows that the reniform nature of the oxygen peaks is not a non-convergence effect. The standard deviations were estimated with the method of Shoemaker, Donohue, Schomaker & Corey (1950).

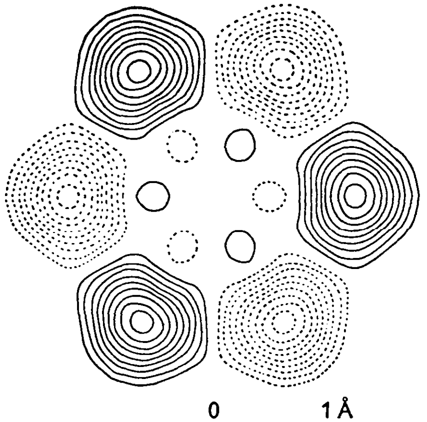

Fig. 1. The function $\varrho(x, y, \frac{1}{4}) - \varrho(x, y, \frac{3}{4})$, made with F_o for calcite. Contours are drawn at intervals of 1 e.Å^{-3}, the zero contour being omitted. Full lines represent positive electron density (at $z = \frac{1}{4}$), broken lines represent negative electron density (at $z = \frac{3}{4}$).

The expression used for calculating the structure factors was:

$$\begin{aligned} F_{hkl} = {} & -6f_0 \sin \pi(l/2) \\ & \times [\exp\{-B_\alpha h^2 - B_\beta (h+2k)^2 - B_\gamma l^2\} \sin 2\pi hx \\ & + \exp\{-B_\alpha k^2 - B_\beta (2h+k)^2 - B_\gamma l^2\} \sin 2\pi kx \\ & - \exp\{-B_\alpha (h+k)^2 - B_\beta (h-k)^2 - B_\gamma l^2\} \sin 2\pi (h+k)x]. \end{aligned}$$

The B_α and B_β were estimated from the shapes of the peaks in the isolation maps. In the case of sodium nitrate, B_α, B_β, and B_γ were also obtained by successive least-squares treatments on the positional parameter simultaneously with the three temperature-factor variables. It is interesting that a preliminary least-squares analysis in which the positional parameter and one isotropic temperature factor were varied resulted in a value for the positional parameter identical with that obtained above. Since B_α and B_β as estimated from the isolation maps were very nearly the same for both crystals, the value of B_γ as obtained by least squares for sodium nitrate was also used for calcite.

Although twenty-two reflections were used in the least-square refinements, it was found that the shifts obtained were not only quite sensitive to the weighting factors used, but also varied if one or two reflections

Table 1. *Parameters in sodium nitrate and calcite*

	x	σ	B_α	B_β	B_γ	Reference
$NaNO_3$	0·24–0·26	—	—	—	—	Wyckoff (1920*a*)
	0·2394	0·0006	—	—	—	Elliott (1937)
	0·242	0·003(?)	—	—	—	Tahvonen (1947)
	0·2402	0·0008	0·0026	0·0030	0·0006	This work
$CaCO_3$	0·24–0·26	—	—	—	—	Wyckoff (1920*b*)
	0·2635	0·0014	—	—	—	Elliott (1937)
	0·2593	0·0008	0·0025	0·0035	0·0006	This work

were omitted during a cycle. The assignment of weighting factors was made in the usual way by assuming the error in F_o was proportional to F_o, or by direct assessment of the error as indicated by the internal consistency of the intensity estimates, or by a combination of these two methods. In an ideal least-squares treatment the parameters should be overdetermined to such an extent that the omission of a single observational equation does not change the result. The Fourier parameters are, therefore, probably more reliable than those obtained by least squares. The final Fourier parameters are presented in Table 1, together with the values reported previously, for comparison. The temperature factors in Table 1, which were obtained by a combination of the Fourier and least-squares results, correspond to r.m.s. displacements, for both substances, of about 0·06, 0·11, and 0·09 Å, parallel to a, perpendicular to a, and parallel to c, respectively.

Observed and calculated structure factors are listed in Table 2.

Table 2. *Observed and calculated structure factors*

	$NaNO_3$		$CaCO_3$	
hkl	F_o	F_c	F_o	F_c
$11\bar{3}$	7·84	−9·16	8·24	−11·31
119	6·01	−6·14	6·88	−7·49
$1,1,\overline{15}$	3·87	−3·64	4·41	−4·32
$12\bar{1}$	6·43	+7·66	6·77	+7·31
125	6·66	−6·87	6·32	−6·46
$12\bar{7}$	5·93	−6·21	5·64	−5·72
1,2,11	4·63	+4·72	4·75	+4·31
$1,2,\overline{13}$	3·66	+4·04	3·78	+3·73
1,2,17	2·90	−3·10	3·61	−2·93
131	$< 0·79$	−0·54	1·07	+0·75
$13\bar{5}$	$< 0·88$	+0·50	1·13	−0·68
137	$< 0·90$	+0·47	$< 0·70$	−0·63
$1,3,\overline{11}$	0·85	−0·35	0·96	+0·53
1,3,13	0·65	−0·31	0·85	+0·48
143	0·81	−0·59	$< 0·64$	+0·15
149	1·67	+0·51	$< 0·46$	−0·14
$15\bar{1}$	2·13	+2·04	*	
$22\bar{3}$	1·12	−1·18	1·13	+1·24
229	0·66	−0·93	$< 0·70$	+0·97
2,2,15	*		$< 0·68$	−0·72
$23\bar{1}$	3·79	−3·55	4·01	−4·00
235	3·58	+3·36	3·78	+3·78
$23\bar{7}$	3·92	+3·18	4·06	+3·56
2,3,11	2·67	−2·24	3·16	−3·17
$2,3,\overline{13}$	2·62	−2·53	3·05	−2·95
241	$< 0·43$	+0·61	$< 0·43$	−0·74
$33\bar{3}$	2·92	−3·26	2·80	−2·02

* Not observed because of experimental conditions.

Discussion

The parameters of Table 1 lead to the following interatomic distances: N–O = 1·218 Å and C–O = 1·294 Å, with standard deviations of 0·004 Å in each case. Within the respective limits of error, the N–O distance found is the same as that found by Elliott, but the C–O distance is 0·021 Å shorter.

The original discussion (Elliott, 1937) of these two distances was concerned with the comparisons between the observed distances in these two ions and those predicted by Pauling, Brockway & Beach (1935). This matter was again discussed by Pauling (1940). The discrepancy that the N–O distance was 0·04 Å shorter than that predicted by the simple valence-bond treatment led to the formulation of the 'formal charge' correction of a decrease in covalent radius (of 0·04 Å) in the case of bonds between atoms where one of them had an effective nuclear charge of +1. That this correction is not of general validity has been apparent for some time, as the results, for example, on methylammonium chloride (Hughes & Lipscomb, 1946) and on several amino acid zwitterions listed by Corey & Pauling (1953), show that the $C–N^+$ distances in these compounds are definitely not shorter than the normal C–N distance of 1·47 Å. Prediction of the N–O distance in the NO_3^- ion, where each N–O bond has one-third double-bond character, is, moreover, unreliable in view of the uncertainty in the value expected for a pure double bond. Pauling's radii (1940, p. 164) give 1·15 Å for this distance, whereas Gordy (1947) predicts 1·20 Å. The situation is further complicated by the fact that the N–O distance in the nitrate ion is about equal to that found in many organic nitro compounds, where each N–O bond has one-half double-bond character, for example: nitromethane, 1·21 Å (Brockway, Beach & Pauling, 1935); tetranitromethane, 1·22 Å (Stosick, 1939); *p*-dinitrobenzene, 1·21 Å (Abrahams, 1950). On the other hand, in the nitrite ion, where again each N–O bond has one-half double-bond character, the distance is longer, viz., 1·24 Å (Carpenter, 1955).

The corresponding situation does not occur in the carbon–oxygen system: the length predicted for one-third double-bond character is 1·288 Å and that predicted for one-half double-bond character is 1·255 Å (Vaughan & Donohue, 1952). These values agree well with the value 1·294 Å found above in calcite, and the values 1·25–1·27 Å found in many carboxylate ions, for example: serine, 1·26 and 1·27 Å (Shoemaker, Barieau, Donohue & Lu, 1953); hydroxyproline, 1·25 and 1·27 Å (Donohue & Trueblood, 1952); threonine, 1·24 and 1·25 Å (Shoemaker *et al.*, 1950); histidine, 1·25 and 1·27 Å (Donohue, Lavine & Rollett, 1956).

The simple valence-bond theory thus accounts satisfactorily for the observed carbon–oxygen distances, but not for the nitrogen–oxygen distances. The latter discrepancies may possibly be connected with the fact that for both the nitrate ion and the nitro group the contributing resonance forms have opposite formal changes on the nitrogen and oxygen atoms. This situation might be expected to shorten the distances from those predicted, as is observed. Precise determination of the N–O bond length in an amine oxide, such as $(CH_3)_3N^+–O^-$ would be of interest on this point.

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A Direct Vector Method for Obtaining Symmetry-Independent Solutions to Crystallographic Problems Applied to Reflections and Single Rotations in Crystals

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By using vector methods within the sixfold system of coordinates that comprise both the direct- and the reciprocal-lattice vectors, the symmetry-independent crystallographic solutions to vector equations are obtained directly. The technique is applied to the study of arbitrary reflections and single rotations in crystals. The symmetry-independent solution to the reflection problem is identical to a recently published solution obtained less directly by the matrix method. The symmetry-independent solution to the rotation problem has not heretofore been given.

Introduction

The treatment of problems in geometrical crystallography by traditional vector methods frequently involves complicated algebraic manipulations which result from the non-orthogonality of the coordinate axes. The solution of some of the problems is simplified by the matrix method. In this method the crystallographic problem is referred to a Cartesian coordinate system by means of a matrix transformation. The problem is then solved in the Cartesian system and the solution is finally referred back to the crystallographic coordinates by a second matrix transformation. The mechanics of solution by either of these