

packing models provides us with a crude picture, but not a dynamic model, for the morphological and mechanical properties of these protein crystals.

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References

- CARLISLE, C. H. & SCOULOU, H. (1951). *Proc. Roy. Soc. A*, **207**, 201.
 DAWSON, I. M. & WATSON, D. H. (1959). *J. Mol. Biol.* **1**, 30.
 FANKUCHEN, I. (1941). *J. Gen. Physiol.* **24**, 315.
 FANKUCHEN, I. (1945). *Advanc. Protein Chem.* **2**, 387.
 HARKER, D. (1957). *Ann. N. Y. Acad. Sci.* **69**, 321.
 KING, M. V., MAGDOFF, B. L., ADELMAN, M. B. & HARKER, D. (1956). *Acta Cryst.* **9**, 460.
 KING, M. V. (1964a). *Biochim. Biophys. Acta* **79**, 388.
 KING, M. V. (1964b). *Nature, Lond.* **201**, 918.
 LABAW, L. W. (1959). *J. Ultrastructure Res.* **3**, 58.
 LABAW, L. W. & WYCKOFF, R. W. G. (1957). *Arch. Biochem Biophys.* **67**, 225.

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Position and Thermal Parameters of Oxygen Atoms in Calcite*

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The position and thermal parameters of the oxygen atoms in calcium carbonate (calcite) at room temperature, 215 °K and 130 °K, have been determined. Reflections to which only oxygen atoms contribute were measured by counter methods. Parameters were refined by least-squares methods. The C–O bond length is 1.283 ± 0.002 at room temperature and does not change significantly between room temperature and 130 °K.

Calcite, one of the polymorphic modifications of calcium carbonate, crystallizes in the rhombohedral system, in space group $R\bar{3}c$, with two molecules of CaCO_3 per unit cell. The carbon atoms and the calcium ions lie along the threefold axis, the former at $0, 0, 0$, and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and the latter at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$. The three oxygen atoms of each carbonate group are arranged symmetrically about the carbon atoms in planes normal to the threefold axis; each oxygen atom lies on a twofold axis. Successive carbonate groups are rotated 180° relative to one another as shown in Fig. 1.

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The carbon atoms and the calcium ions are in body centered positions. The atomic arrangement deviates from a completely body centered one only by virtue of 60° rotations of successive carbonate groups about the body diagonal; *i.e.* oxygen atoms are not in body centered positions. As a result, only the oxygen atoms contribute to reflections with indices of the type $h+k+l=2n+1$.

The calcite structure may be conveniently described in terms of a triply primitive hexagonal unit cell with $a=4.990$ and $c=17.00 \text{ \AA}$ (at room temperature). There is only one variable position parameter: that of an oxygen atom in one of the (*e*) positions of the hexagonal cell:

$$x, 0, \frac{1}{4}; \quad 0, x, \frac{1}{4}; \quad \bar{x}, \bar{x}, \frac{1}{4}; \quad \bar{x}, 0, \frac{3}{4}; \quad 0, \bar{x}, \frac{3}{4}; \quad x, x, \frac{3}{4}.$$

The length of the C–O bond, which has been the subject of many experimental investigations, is deter-

mined by this parameter. In spite of the simplicity of the structure and the importance of an accurate knowledge of the C-O bond length in the carbonate ion, the position parameter of the oxygen atom in calcite had been determined only approximately prior to 1957. Bragg (1914) had reported $x=0.25$ to 0.27 ; subsequently Schiebold (1919), Wyckoff (1920) and Elliott (1937) reported values ranging from 0.255 to 0.31 , corresponding to C-O bonds from 1.27 to 1.55 Å long.

Sass, Vidale & Donohue (1957) (referred to as SVD below) published the results of a detailed study of the position and thermal parameters of the oxygen atoms in calcite and sodium nitrate. Their results will be discussed below.

The present investigation was begun before the SVD results were published. Completion of our work has been delayed and this has enabled us to carry out detailed refinements of our data using modern computing techniques.

Experimental

The indices of reflections which, in the rhombohedral system, are of the type $h+k+l=2n+1$, transform to the type h, k, l with $l=2n+1$ in the hexagonal system. In the present work the intensities of fifty such "oxygen" reflections were measured with a scintillation counter mounted on a Weissenberg camera base, as radiation

detector. Filtered Cu $K\alpha$ and Mo $K\alpha$ radiations were used. Measurements were made on two approximately spherical crystals about 0.2 mm in diameter; one was mounted for rotation about the a axis; the other was mounted along c . Intensity data were corrected for absorption. The average deviation of intensities in either set from the corresponding mean values for both sets was less than 4% . In assessing the above, it should be noted that almost all of the reflections considered were of low intensity and consequently difficult to measure with high precision.

In addition to the room temperature measurements, 37 of the reflections were measured at temperature intervals of about 10°C between room temperature and -140°C , with Mo K radiation. Thirteen of the reflections that were measured at room temperature were too weak to be measured with useful precision when Mo K radiation was used.

The crystals were cooled by blowing cold nitrogen gas over them. Crystal temperatures were measured using a thermocouple placed in the cold stream immediately adjacent to the crystal but just outside the X-ray beam. Values of F_{obs} applicable to 215°K and 130°K were derived from smoothed plots of F_{obs} vs temperature for each reflection. The three sets of F_{obs} are listed in Table 1.

Table 1. Calcite: F_{obs} and F_{calc} - 'oxygen' reflections

hkl	(Max Data)								
	300°K		215°K		130°K				
	F_{obs}	F_{calc}	F_{obs}	F_{calc}	F_{obs}	F_{calc}	F_{obs}	F_{calc}	
113	10.51	11.86	10.88	12.22	11.32	12.38			
9	7.10	-7.59	7.39	-7.93	7.66	-8.17			
15	4.18	4.98	4.51	4.40	4.80	4.69			
21	2.36	-2.42	2.90	-2.73	3.15	-3.07			
27	1.66	1.58	1.85	1.89	2.19	2.29			
12 $\bar{1}$	8.12	7.98	8.31	8.23	8.45	8.41			
5	7.26	-7.11	7.42	-7.33	7.60	-7.53			
7	6.18	-6.04	6.46	-6.32	6.68	-6.53			
11	4.77	4.67	4.97	4.88	5.21	5.12			
13	3.83	3.66	4.01	3.99	4.28	4.19			
17	3.05	-2.91	3.37	-3.14	3.54	-3.44			
19	2.30	-2.24	2.63	-2.53	2.90	-2.82			
23	1.89	1.97	2.21	2.22	2.53	2.58			
15 $\bar{1}$	3.11	2.93	3.57	3.35	3.89	3.70			
2	2.92	-2.82	3.31	-3.25	3.73	-3.62			
4	2.60	-2.69	3.20	-3.11	3.60	-3.47			
11	2.47	2.45	2.86	2.88	3.12	3.26			
13	2.25	2.26	2.64	2.66	3.09	3.05			
17	1.88	-1.97	2.30	-2.39	2.73	-2.84			
19	1.63	-1.76	2.12	-2.15	2.54	-2.57			
16 $\bar{1}$	1.75	-1.88	2.10	-2.17	2.42	-2.48			
5	1.81	1.76	2.10	2.04	2.42	2.34			
7	1.67	1.62	1.94	2.11	2.30	2.45			
11	1.36	-1.50	1.65	-1.78	2.01	-2.09			
23 $\bar{1}$	4.43	-4.28	4.71	-4.54	4.97	-4.75			
2	3.94	3.87	4.18	4.17	4.40	4.39			
7	4.04	3.85	4.27	4.10	4.50	4.33			
11	2.96	-2.94	3.30	-3.16	3.56	-3.51			
13	3.26	-3.05	3.51	-3.30	3.65	-3.59			
17	2.05	2.13	2.36	2.47	2.70	2.77			
19	2.34	2.33	2.65	2.60	2.94	2.96			
23	1.35	-1.49	1.69	-1.83	2.03	-2.16			
29	1.75	-1.69	1.91	-1.97	2.65	-2.40			
253	2.43	2.38	2.74	2.63	3.06	2.85			
9	2.42	-2.03	2.69	-2.30	2.88	-2.55			
333	2.18	-2.33	2.53	-2.67	2.84	-3.00			
9	2.13	2.06	2.35	2.38	2.58	2.73			
R	3.6%		2.3%		2.9%				

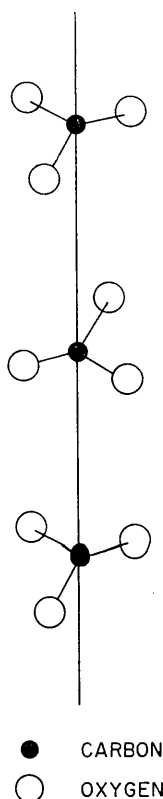


Fig. 1. Arrangement of atoms about the threefold axis in calcite. Open circles: oxygen; filled circles: carbon.

The coefficients of thermal expansion in the range from 110° to 300°K were also measured. Single crystals were mounted for this purpose on a Norelco diffractometer adapted for single-crystal measurements. Filtered Cr $K\alpha$ radiation was used. Measurements of the reflection angles of 300 and 00.12 at small temperature

intervals yielded values of $\alpha_a = -3.2 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$; $\alpha_c = 25.0 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$ (Table 2). Within experimental error the coefficients were constant over the temperature range investigated. Our results agree well with those reported by Voigt (1928) (based on dilatometric measurements): $\alpha_a = -5.75 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$; $\alpha_c = 25.6 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$.

Table 2. *Thermal expansion: calcite*

<i>T</i>	<i>a</i>	<i>c</i>
110°K	4.9930 ± 0.0003 Å	16.917 ± 0.002 Å
175°	4.9923 ± 0.0003	16.943 ± 0.002
240°	4.9910 ± 0.0003	16.972 ± 0.002
300°	4.9900 ± 0.0002	17.002 ± 0.001

The fifty room temperature reflections (Table 3) were subjected to least-squares analysis with the Busing-Levy program (Busing & Levy, 1959, 1962.) The variable parameters include the scale factor, the *x* coordinate of one oxygen atom and its four independent temperature factors (two temperature factors are fixed by symmetry since the oxygen atom lies on a twofold rotation axis).

Table 3. *Calcite - 'oxygen' reflections (300°K)*
(Mo K α and Cu K α data)

<i>HKL</i>	<i>F</i> _{obs}	<i>F</i> _{calc}
113	10.56	11.87
119	7.39	-7.59
1,1,15	4.34	4.07
1,1,21	2.38	-2.40
1,1,27	1.67	1.55
12 $\bar{1}$	8.23	7.93
125	7.34	-7.12
127	6.22	-5.96
1,2,11	4.80	4.70
1,2,13	3.86	3.57
1,2,17	3.07	-2.95
1,2,19	2.31	-2.15
1,2,23	1.90	1.99
15 $\bar{1}$	3.13	2.98
155	2.94	-2.87
157	2.82	-2.76
1,5,11	2.49	2.49
1,5,13	2.26	2.34
1,5,17	1.89	-2.01
1,5,19	1.64	-1.83
161	1.76	-1.87
165	1.82	1.73
167	1.68	1.83
1,6,11	1.37	-1.48
23 $\bar{1}$	4.45	-4.38
235	3.96	3.92
237	4.06	3.99
2,3,11	2.97	-2.93
2,3,13	3.00	-3.13
2,3,17	2.06	2.10
2,3,19	2.35	2.44
2,3,23	1.36	-1.44
2,3,25	1.76	-1.78
253	2.44	2.46
259	2.43	-2.05

Table 3 (cont.)

<i>HKL</i>	<i>F</i> _{obs}	<i>F</i> _{calc}
333	2.19	-2.18
339	2.14	2.07
223	0.87	-1.01
229	0.76	0.78
2,2,15	0.50	-0.52
131	0.59	0.69
135	1.11	-1.00
137	0.49	-0.22
1,3,11	1.01	1.00
1,3,13	0.25	-0.10
143	0.27	0.28
143		0.04
149	0.43	-0.41
149	0.28	-0.18
241	0.72	-0.62
245	0.67	0.65

R = 4.4 %

Individual terms were weighted as follows for the least-squares analysis: $w^2 = 1/\sigma(F)$, with $\sigma F = 0.0490 + 0.0255F$. The estimated errors thus run from about 3% for the stronger reflections to about 5% for the weaker ones. The reasonableness of the overall scale of weights (as well as the estimation of the reliability of the data) was attested by the fact that the sum of the squares of deviations divided by the number of degrees of freedom ranged from 1.0 to 1.1; the expected value for a perfectly accurate estimate is unity.

Similar methods were used to refine the three sets of Mo K α data (300°, 215° and 130°K). In all cases, refinements were continued until there were no further changes in any of the variable parameters in the seven decimal places used in the calculations.

Some difficulty was experienced in refining the low temperature data. As the calculations progressed, b_{11} for both 152°K and 130°K persistently acquired negative values. To check on the possibility that this was caused by a fortuitously bad choice of weights, one cycle of refinement was run with unit weights; furthermore, the 113 reflection, which may suffer substantially from extinction, was omitted from the new calculations. The results did not differ significantly from those for the graded weights and it appeared likely that the fault lay in the data rather than in the system of weights used.

The following procedure was then used. The room temperature results, based on all fifty reflections listed in Table 3, were assumed to be 'correct'. Refinement of the low temperature data was then based, not on the absolute values of the low temperature measurements, but on the *differences* between those and the room temperature values.

It was felt that systematic errors would be minimized by this procedure. This, indeed, appeared to be the case. Refinements based on differences as described above yielded discrepancy factors of 2.3% for the 215° data and 2.9% for the 130° data as compared with 4.2

and 3.8% for the conventional calculations*. The b_{11} temperature factor remained well behaved at 215° but again acquired negative values at 130°K. The causes of this behavior could not be established unambiguously; it seems to be related to the small absolute magnitude of b_{11} , and the small number of independent hk sets of reflections used in the analysis. The fifty room-temperature reflections represent eleven independent hk sets; the 37 reflections used in the low temperature work represent only seven such sets. Evidently the seven sets did not furnish enough "redundancy" for the least-squares analysis in all cases. Results of the analysis of the three groups of data are shown in Table 4.

Discussion

It is useful first to compare our results with those reported by SVD. The latter measured twenty independent reflections with odd l indices, using filtered Cu K radiation; intensities were recorded on film. Their results may be summarized as follows: $x(0) = 0.2593 \pm 0.0008$, implying a C-O bond length of 1.294 ± 0.004 Å. Three temperature factors were computed, corresponding to r.m.s. thermal displacements of the oxygen atom of 0.06, 0.11 and 0.09 Å parallel to a , b^* and c respectively.

Our results indicate a C-O bond length of 1.283 ± 0.002 Å. The difference between our value and SVD's equals six of our standard deviations and is clearly significant. Agreement between our temperature factors and those reported by SVD is somewhat better, but significant differences do exist and these are attributable, in part, to two factors. First, SVD attempted to describe the temperature motion of the oxygen atom in terms of only three parameters. The

* It may be useful to spell out the procedure used to calculate R for these two sets of low temperature data. The room temperature data listed in Table 3 were refined in the usual way. The assumption was made that the calculated parameters as well as F_{calc} were "correct" and that differences between F_{obs} and F_{calc} were due to systematic experimental errors. These differences were then subtracted from the corresponding F_{obs} of the low temperature sets to yield F'_{obs} . The listed values of R were computed in the usual way with the use of these F'_{obs} and F_{calc} .

oxygen atom lies on a twofold axis and this reduces the number of independent thermal parameters from six, for the general case, to four, not three parameters. Also SVD used Cu $K\alpha$ radiation exclusively. For the study of temperature motions in a substance like calcite, in which the amplitudes of thermal motion are relatively small, the use of shorter wavelengths offers obvious advantages.

SVD showed that, in calcite-type structures, a Fourier summation using as coefficients the structure factors of terms with odd l indices (oxygen reflections) is equivalent to a difference electron-density map in which $\rho(xy\frac{1}{2})$ is subtracted from $\rho(xy\frac{3}{4})$. Since $\rho(xy\frac{3}{4})$ differs from $\rho(xy\frac{1}{4})$ only by a rotation of a carbonate ion by 60° (Fig. 1), the difference map shows positive and negative oxygen peaks at 60° intervals about the origin. The symbol ρ^* is used to indicate the 'electron density' in these maps.

SVD computed such a difference map and noted that the electron density contours in the oxygen appeared to be kidney-shaped, as though curved about a center of oscillation. This reniform shape of the oxygen contours led the authors to conclude that oscillatory

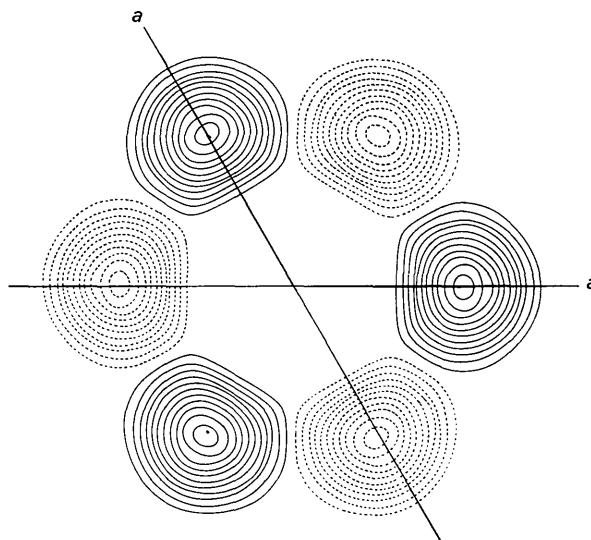


Fig. 2. $\rho(xy\frac{1}{4}) - \rho(xy\frac{3}{4})$: 20 terms

Table 4. Position and thermal parameters of oxygen in calcite

	300°K	215°K	130°K
x	0.25706 ± 0.00033	0.25708 ± 0.00038	0.25696 ± 0.00049
C-O(Å)	1.283 ± 0.002	1.283 ± 0.002	1.282 ± 0.002
b_{11}	0.00524 ± 0.00059	0.00434 ± 0.00054	$-0.00173 \pm 0.00070^*$
b_{22}	0.01775 ± 0.00090	0.01273 ± 0.00083	0.00867 ± 0.00104
b_{33}	0.00104 ± 0.00005	0.00088 ± 0.00003	0.00063 ± 0.00004
b_{23}	-0.00218 ± 0.00019	-0.00169 ± 0.00018	-0.00165 ± 0.00123
(r_l^2)	0.00101 ± 0.00080	0.00146 ± 0.00080	$-0.00056 \pm 0.00090^*$
$(r_l^2)^{\frac{1}{2}}$ (Å)	0.032*	0.038	—
$(r_{II}^2)^{\frac{1}{2}}$	0.089 ± 0.007	0.078 ± 0.007	0.051 ± 0.008
$(r_{III}^2)^{\frac{1}{2}}$	0.155 ± 0.004	0.137 ± 0.004	0.122 ± 0.004
$\alpha(^{\circ})$	47.8 ± 2.1	43.1 ± 2.1	42.6 ± 2.6
$R(\text{Cu plus Mo})$	4.4%	—	—
$R(\text{Mo data})$	3.6%	2.3%	2.9%

* b_{11} was not positive definite at 130°K: standard deviations of $(r_l^2)^{\frac{1}{2}}$ are therefore of doubtful value.

motion of the oxygen atoms about the c axis was being displayed on the ϱ^* map.

We have computed ϱ^* maps using our F_{obs} as coefficients. In the first case, we restricted the summation to the twenty independent terms used by SVD. The map is shown in Fig. 2. In agreement with the SVD observation, there is some indication of reniform character, of curvature of the contours about the origin.

The calculation was then repeated with all fifty (Mo $K\alpha$ +Cu $K\alpha$) F_{obs} 's as coefficients, and these results are shown in Fig. 3. Reniform character of the electron density contours is not detectable; its presence in Fig. 2 and in the SVD map is probably a computational artifact arising from the use of an insufficient number of terms in the summation.

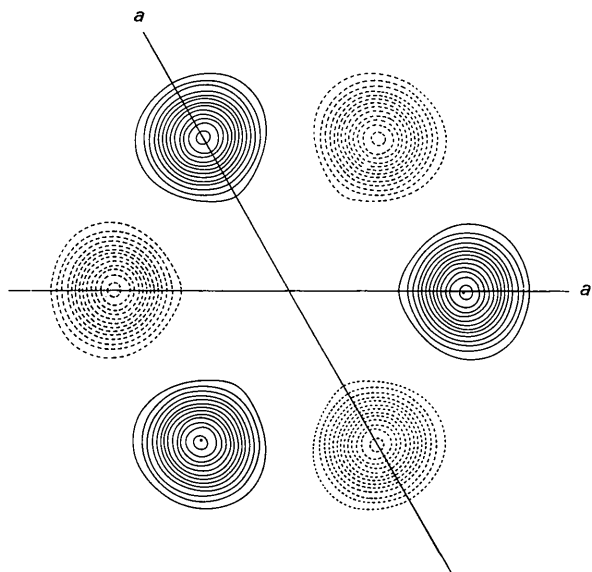


Fig. 3. $\varrho(xy\frac{1}{2}) - \varrho(xy\frac{3}{2})$: 50 terms

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Localisation des Atomes d'Hydrogène dans l'Acide Adipique $\text{COOH}[\text{CH}_2]_4\text{COOH}$

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The crystal structure of adipic acid has been recomputed to determine the positions of hydrogen atoms. Crystals of $\text{COOH}[\text{CH}_2]_4\text{COOH}$ are monoclinic, space group $P2_1/c$, 2 molecules in a unit cell with lattice constants $a = 10.01$, $b = 5.15$, $c = 10.06$ Å, $\beta = 136^\circ 45'$. Least-squares refinement on 380 visually estimated intensities was used to obtain optimum values for positional and thermal parameters. The value of R is 8%.

Introduction

Nous nous proposons d'étudier les propriétés physiques des monocristaux de diacides saturés jusqu'à l'acide tétradécanedioïque ($\text{COOH}[\text{CH}_2]_{12}\text{COOH}$). Dans le

In the present work efforts have also been made to determine the shape and orientation of the thermal ellipsoid of the oxygen atom in calcite as a function of temperature. One principal axis of the ellipsoid (r_I) coincides with the a axis of the unit cell by symmetry. The other two principal axes (r_{II} and r_{III}) lie in the plane normal to a . To specify their orientation, an angle α is defined as the angle which the long axis of the ellipsoid makes with the c axis. This measurement is made from the positive c direction towards the negative b^* direction.

The magnitudes of the principal axes of the ellipsoid at three temperatures are listed in Table 4. In view of the anomalous behavior of b_{11} at 130°K, and the large error in b_{11} at other temperatures, little can be said about the variation of (r_I) with temperature. (r_{II}) and (r_{III}) increase in length with increasing temperature, as expected. The angle α appears to increase slightly between 130°K and room temperature. The C–O bond length does not change significantly in the temperature range studied.

References

- BRAGG, W. L. (1914). *Proc. Roy. Soc. A*, **89**, 68.
 BUSING, W. R. & LEVY, H. A. (1959). *A Crystallographic Least Squares Refinement Program for the IBM 704*. ORNL-59-4-37, Oak Ridge National Laboratory.
 BUSING, W. R., MARTIN, K. & LEVY, H. A. (1962). *ORFLS, A FORTRAN Crystallographers Least Squares Program*. ORNL-TM-305, Oak Ridge National Laboratory.
 ELLIOTT, N. (1937). *J. Amer. Chem. Soc.* **59**, 1380.
 SASS, R. L., VIDALE, R. & DONOHUE, J. (1957). *Acta Cryst.* **10**, 567.
 SCHIEBOLD, E. (1919). *Abh. sächs. Ges. (Akad.) Wiss. Math.-Phys. Kl. Nr. 2*, 68.
 VOIGT, W. (1928). *Lehrbuch der Kristallphysik*. Leipzig & Berlin: Teubner.
 WYCKOFF, R. W. G. (1920). *Amer. J. Sci.* **50**, 317.

cadre de cette étude nous avons déterminé la structure cristalline des acides subérique et azélaïque. (Housty & Hospital, 1964).

La structure de l'acide adipique a déjà été faite par MacGillavry (1928) puis reprise par Morrison & Ro-