

à trois atomes d'iode, les liaisons Sm-I sont toutes égales et ont pour valeur 3,29 Å, valeur supérieure à la somme des rayons ioniques Sm-I.

Un atome d'iode est entouré par trois atomes de samarium, trois atomes de soufre et trois autres atomes d'iode, les liaisons I-S et I-I ont des longueurs respectivement égales à 3,80 Å et 4,32 Å. On observe également des contacts entre atomes de soufre, la distance entre ces atomes est de 3,34 Å, valeur plus faible que la valeur normale dans les sulfures: 3,64 Å

Les distances interatomiques, à l'intérieur des couches (SmS)_n sont plus courtes que les liaisons qui ont été obtenues dans les sulfures de samarium; au contraire les liaisons entre ces feuillets et les couches d'iode sont plus longues que celles que l'on attendrait normalement; cette constatation nous conduit à envisager la structure de SmSI comme résultant de l'empilement de feuillets dans lesquels la terre rare est fortement liée à l'anion de plus forte électronégativité, le soufre. Ces feuillets (SmS)_n sont séparés par de doubles couches d'iode, le cation étant bien moins fortement lié à l'anion de moins forte électronégativité, l'iode.

Une étude actuellement en cours sur les halogénosulfures de terres rares entreprise par Dagrón & Thevet (1971), montre que tous les composés étudiés ont une structure en feuillets contenant des tétraèdres (L₄S) arrangés suivant deux types de symétrie:

– soit quadratique comme pour CeSi, Etienne (1969); la maille fait intervenir l'empilement de deux feuillets, et l'on observe une structure voisine de PbFCI,

– soit hexagonale (type SmSI): il faut superposer trois feuillets pour obtenir la maille.

Références

- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
 BUSING, W. R., MARTIN, K. D. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 DAGRON, C. (1966). *C. R. Acad. Sci. Paris, Sér. C* **262**, 1575–1576.
 DAGRON, C. & THEVET, F. (1971). *Ann. Chim.* **6**, 67–81.
 ETIENNE, J. (1969). *Bull. Soc. Franç. Minér. Crist.* **92**, 134–140.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151–512.

Acta Cryst. (1973). **B29**, 347

Prediction of Units Cells and Atomic Coordinates for the n-Alkanes

BY S. C. NYBURG AND J. A. POTWOROWSKI

Lash Miller Chemical Laboratories, University of Toronto, Toronto 181, Ontario, Canada

(Received 14 June 1972; accepted 16 October 1972)

The n-alkanes, C_{2n}H_{2n+2}, with n > 6 crystallize in four isostructural sets according to the magnitude and parity of n. Given the structure of any one ('key') alkane in the set the cell dimensions and structures of the others can be predicted. The method assumes that the vector from the midpoint of the outermost C–C bond to (0, 0, ½) is of fixed length and parallel throughout all members of the set.

The n-alkanes C_nH_{2n+2} (n ≥ 6) crystallize in one of three systems, triclinic [n(even) ≤ 26] (Müller & Lonsdale, 1948), monoclinic or, if not quite pure, orthorhombic [26 ≤ n(even) ≤ 36] and orthorhombic [11 ≤ n(odd) ≤ 39] (Broadhurst, 1962).

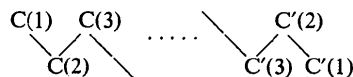
Within each system the long spacings d(001) change smoothly with n, strongly indicative of isostructurality and, for each of the four types listed above, the detailed structure of a key member is known: n-even triclinic, C₁₈H₃₈ (Nyburg & Lüth, 1972), n-even monoclinic, C₃₆H₇₄ (Shearer & Vand, 1956), n-even orthorhombic, C₃₆H₇₄ (Teare, 1959) and n-odd orthorhombic, C₂₃H₄₈ (Smith, 1953, 1972). It is possible from each of these key structures to predict the unit-cell dimensions and structures of the other members.

Prediction of cell dimensions and structures is based simply on the fact that one assumes that the carbon chain (in every case a flat, linear zigzag) preserves its orientation with respect to the crystallographic axes

for each member of the series within the stated limits on n. If one chooses the longest cell dimension (traditionally c) to lie as close as possible to the molecular axis it seems safe to assume that the cell parameters a, b and γ will not change greatly within the group. This is rigorously so for the orthorhombic members (measured variations in a and b being of order ½%) since the chain lies exactly along c to satisfy symmetry requirements.

Cell dimensions

For the triclinic n-even members (space group P $\bar{1}$) and monoclinic members (P2₁/a) the molecules are centered on $\bar{1}$ so that the carbon numbering on the chain is conveniently C(1), C(2)···C(n/2), C'(n/2)···C'(2), C'(1).



The chain direction is given by the vector whose termini are the midpoint of bond C(1)–C(2), called the point (1,2), and the midpoint of bond C'(1)–C'(2). The length of this vector is $\frac{1}{2}(n-2)$ ethylene groups.

Consider, Fig. 1, for any known structure, the vector \mathbf{v} from (1,2) to $(0,0,\frac{1}{2})$. For any other member of the group one finds simply the new length of the chain by proportion and, by adding \mathbf{v} to the new point (1,2), finds the new position of $(0,0,\frac{1}{2})$. Hence the new cell parameters.

The results depend, of course, upon the accuracy with which the key structure is known within each group. The satisfactory agreement found with observed cell parameters (or, where these have not been determined, with long spacings) shows that these structures are known sufficiently accurately for our purpose.

In orthogonal axes (\mathbf{X} along \mathbf{x} , \mathbf{y} in the \mathbf{xy} plane, \mathbf{Z} along \mathbf{z}^* , Fig. 1) let (1,2) have coordinates X, Y, Z . Let the orthogonal coordinates of $(0,0,\frac{1}{2})$ be $X_{c/2}, Y_{c/2}, Z_{c/2}$ then \mathbf{v} is $(X_{c/2}-X, Y_{c/2}-Y, Z_{c/2}-Z)$. Using a key structure of n carbon atoms to predict the structure for n' (same parity) carbon atoms we scale the coordinates of (1,2) by $(n'-2)/(n-2)$. To these new coordinates we add \mathbf{v} to obtain the coordinates $X'_{c/2}, Y'_{c/2}, Z'_{c/2}$ for $(0,0,\frac{1}{2})$ of the new cell. The c dimension of the new cell is obtained directly from the orthogonal coordinates of $(0,0,\frac{1}{2})$, $d(001)$ from $2Z'_{c/2}$ and α and β from the cosine rule.

The orthogonal coordinate $Z'_{c/2}$ of $(0,0,\frac{1}{2})$ is linearly dependent on n' , namely

$$Z'_{c/2} = \frac{n'-2}{n-2} Z + (Z_{c/2} - Z).$$

But $Z'_{c/2}$ is $d(001)/2$ whence, after rearrangement

$$d(001) = 2 \frac{Zn'}{n-2} + 2 \left(Z_{c/2} - \frac{Zn}{n-2} \right). \quad (1)$$

Atomic coordinates

Given the positions of C(1), C(2) and their attached hydrogen atoms for one member of the series the positions of all the other atoms in the chain can be found by linear interpolation.

Results

(i) Triclinic, $P\bar{1}$

The cell having the chain axis as close as possible to the z axis for the key structure, $C_{18}H_{38}$, is: $a=4.285$, $b=4.82$, $c=24.90$ Å, $\alpha=85.15$, $\beta=67.80$, $\gamma=72.70^\circ$ (Nyburg & Lüth, 1972).

The orthogonal coordinates found for C'(1) and C'(2) are (in Å): (3.409, -1.589, 10.155) and (2.978, -0.628, 9.045) giving X, Y, Z for (1,2) as (3.194,

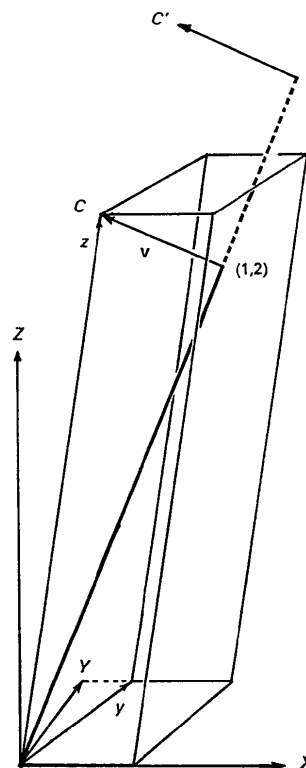


Fig. 1. Triclinic cell showing (1,2) midpoint of bond C(1)–C(2) and vector \mathbf{v} to C at $(0,0,\frac{1}{2})$. The broken line shows the extension of the molecular backbone to another alkane of the series and the vector shows the prediction of the new cell point $(0,0,\frac{1}{2})$ labelled C'.

Table 1. Triclinic (n -even) series of alkanes

| Prediction of cell parameters c , α , and β based on those for $C_{18}H_{38}$ (Nyburg & Lüth, 1972). | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|---------|
| n | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| c (Å) | 9.83 | 12.31 | 14.81 | 17.32 | 19.84 | 22.37 | (24.90) |
| α (°) | 76.67 | 79.51 | 81.40 | 82.75 | 83.75 | 84.53 | (85.15) |
| β (°) | 62.02 | 63.91 | 65.20 | 66.13 | 66.82 | 67.37 | (67.0) |
| n | 20 | 22 | 24 | 26 | 28 | 30 | 32 |
| c (Å) | 27.43 | 29.97 | 32.50 | 35.04 | 37.58 | 40.12 | 42.66 |
| α (°) | 85.66 | 86.08 | 86.43 | 86.73 | 87.00 | 87.23 | 87.43 |
| β (°) | 68.16 | 68.46 | 68.71 | 68.92 | 69.11 | 69.27 | 69.42 |
| n | 34 | 36 | | | | | |
| c (Å) | 45.20 | 47.75 | | | | | |
| α (°) | 87.61 | 87.77 | | | | | |
| β (°) | 69.54 | 69.66 | | | | | |

–1.108, 9.600). The orthogonal coordinates $X_{c/2}$, $Y_{c/2}$, $Z_{c/2}$ of $(0, 0, \frac{1}{2})$ for $C_{18}H_{38}$ are (4.703, –0.363, 11.521) whence the vector \mathbf{v} is (1.509, 0.745, 1.921).

The results obtained for c , α and β for the triclinic series are given in Table 1, Fig. 2. Three sets of cell dimensions other than those for $C_{18}H_{38}$ are known, those of C_6H_{14} (Norman & Mathisen, 1961a)* of C_8H_{18} (Norman & Mathisen, 1961b; Mathisen, Norman & Pedersen, 1967) and of $C_{20}H_{42}$ (Crissman, Passaglia, Eby & Colson, 1970). The observed cell dimensions, in each case transformed to match those of $C_{18}H_{38}$, are given in Table 2. The relative constancy of a , b and γ should be noted and the results obtained for c , α and β should be compared with those in Table 1. The largest angular discrepancy is for α of C_6H_{14} (obs: 77.73°, calc: 76.67°). This, the smallest known member of the triclinic series, might be expected not to be accurately isostructural with the others because of the more important influence of molecular end effects. However it is sufficiently isostructural, as we see below, for a remarkably accurate set of atomic coordinates to be predicted.

* The cell dimensions cited by Wyckoff (1966) appear to be an earlier preliminary set of Norman & Mathisen, 1960; the atomic coordinates are, however, correct.

Table 2. Observed cell dimensions of triclinic n -even alkanes transformed to axial system for $C_{18}H_{38}$

| n | 6 | 8 | 20 |
|--------------|-------|-------|-------|
| a (Å) | 4.17 | 4.22 | 4.28 |
| b (Å) | 4.70 | 4.79 | 4.82 |
| c (Å) | 9.71 | 12.19 | 27.14 |
| α (°) | 77.73 | 80.31 | 85.76 |
| β (°) | 61.81 | 64.14 | 68.31 |
| γ (°) | 75.00 | 74.20 | 72.65 |

Individual cell dimensions do not seem to have been measured for members of the series other than those given above. However many of the long spacings are known and these are compared with predicted values in Table 5. Broadhurst (1962) gives the empirical relation between n' and $d(001)$ as $1.219n' + 1.28$ (in Å). Using $Z = 9.600$ and Z_c as 11.521 Å we obtain, from (1) above, $d(001) = 1.200n' + 1.44$ (Å).

Atomic coordinates

We predict atomic coordinates for C_6H_{14} as an example. The cell dimensions are (Norman & Mathisen, 1961a) $a = 4.17$, $b = 4.70$, $c = 8.57$ Å, $\alpha = 96.6^\circ$, $\beta = 87.2^\circ$, $\gamma = 105.0^\circ$. Transformation to a new (primed) cell as follows $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = \mathbf{a} + \mathbf{c}$ (i.e. by a 100/010/101 transformation, *International Tables for X-ray Crystallography*, 1952) gives the values cited in Table 2. Assuming $a = 4.285$, $b = 4.820$ Å and $\gamma = 72.0^\circ$ the remaining predicted parameters are given in Table 1. The transformed atomic coordinates (primed) are given by $\mathbf{x}' = \mathbf{z} - \mathbf{x}$, $\mathbf{y}' = \mathbf{y}$, $\mathbf{z}' = -\mathbf{z}$. The coordinate data are given in Table 3 and illustrated in Fig. 3. For comparison the predicted and actual cells have been superimposed at their central centres of symmetry and given a slight relative rotation. The correspondence between observed and predicted structure is striking.

(ii) Monoclinic, $P2_1/a$

The key structure is $C_{36}H_{74}$ (Shearer & Vand, 1956), cell dimensions $a = 5.57$, $b = 7.42$, $c = 48.35$ Å, $\beta = 119.1^\circ$ with two molecules per cell, one of which is centred at the origin. We assume both molecules to lie parallel to the B face. Renumbering the atoms to fit in with the above scheme, Shearer & Vand's data give the orthogonal X , Z coordinates of C(1) as $(-10.52, 19.63)$ and of C(2) as $(-9.36, 18.77)$ yielding (1, 2) as $(-9.94, 19.20)$. The orthogonal coordinates of $(0, 0, \frac{1}{2})$ are $(-11.76, 21.12)$ whence \mathbf{v} is $(-1.82, 1.92)$ (in Å).

Table 3. Structure of C_6H_{14}

Experimental coordinates from Norman & Mathisen (1961a) (N & M) $\times 10^4$ for carbon and $\times 10^3$ for hydrogen. (i) Nomenclature of N & M; (ii) Nomenclature this paper; (iii) Fractional coordinates of N & M; (iv) as (iii) after transformation; (v) predicted.

Apart from H_1 , N & M gave only 'average' positions for the pairs of hydrogen atoms on each carbon atom.

| i | ii | iii | x | | iii | y | | iii | z | |
|------------|-------|------|-----|------|------|------|------|------|-------|-------|
| | | | iv | v | | iv | v | | iv | v |
| C1 | C(1) | 2795 | 687 | 528 | 2322 | 2322 | 2342 | 3482 | -3482 | -3417 |
| C2 | C(2) | 1366 | 787 | 954 | -65 | -65 | -4 | 2153 | -2153 | -2149 |
| C3 | C(3) | 723 | -59 | -213 | 1180 | 1180 | 1173 | 664 | -664 | -634 |
| H_1 | HT | — | — | 140 | 146 | 146 | 136 | 428 | -428 | -445 |
| H_2, H_3 | — | — | — | — | 356 | 356 | — | 335 | -335 | — |
| | H2(1) | — | — | 214 | — | — | 386 | — | — | -364 |
| | H3(1) | — | — | -226 | — | — | 345 | — | — | -302 |
| H_4, H_5 | — | — | — | — | -131 | -131 | — | 223 | -223 | — |
| | H2(2) | — | — | 375 | — | — | -111 | — | — | -225 |
| | H3(2) | — | — | -65 | — | — | -152 | — | — | -193 |
| H_6, H_7 | — | — | — | — | 248 | 248 | — | 57 | -57 | — |
| | H2(3) | — | — | 139 | — | — | 269 | — | — | -85 |
| | H3(3) | — | — | -300 | — | — | 228 | — | — | -23 |

space group $Pbcm$. Because the molecules have to lie parallel to z the orthorhombic cases are trivial. Only z coordinates of the end carbon atom are needed for predictive purposes. Smith (1972) gives c as 62.31 Å and Z coordinates of C(1) and of C(2) calculated as 1.573 and 2.848, whence (1,2) has $Z=2.2105$ Å.

The number of ethylene groups between this point and the molecular centre $z=\frac{1}{4}$ is $\frac{3}{4}$. The distance be-

tween the molecular centre and (1,2) is $\frac{1}{4}(62.31) - 2.2105 = 13.367$ Å. Thus the c cell dimension for n' odd is

$$4 \frac{(n'-2)}{21} 13.367 + 2.2105 = 2.546n' + 3.75 \text{ Å}.$$

Broadhurst (1962) gives $c/2$ as $d(001)$ so that half the above values, namely $1.273n' + 1.875$, should be compared with his $1.27n' + 1.98$ (Broadhurst, Fig. 3). Measured and predicted values are given in Table 5.

The derivation of atomic coordinates for any other member of the series could be easily derived from the fractional coordinates of C(1) and of C(2) for $C_{23}H_{48}$, which are (0.1931, 0.03362, 0.02525) and (0.3123, 0.1162, 0.0457) (Smith 1972).

(iv) Orthorhombic n -even

The key structure is $C_{36}H_{74}$ (Teare, 1959), space group $Pca2_1$, $c=95.14$ Å. The Z coordinates of C(1) and of C(2) are 1.558 and 2.829 Å whence (1,2) has Z of 2.194 Å. The number of ethylene groups between (1,2) and the molecular centre at $z=\frac{1}{4}$ is $\frac{3}{4}$. The distance between (1,2) and the molecular centre is

$$\frac{1}{4}(95.14) - 2.1935 = 21.592.$$

Thus the c dimension for an n' even chain is

$$4 \frac{(n'-2)}{34} 21.592 + 2.194 = 2.540n' + 3.693.$$

Half these values, $1.270n' + 1.840$ are also given in Table 5 for comparison with known values. The empirical equation given by Broadhurst (1962) for these is the same as for the n -odd series. Atomic coordinates for any other member of the series can be readily be obtained from the atomic coordinates of C(1) and of C(2) given for $C_{36}H_{74}$ by Teare (1959).

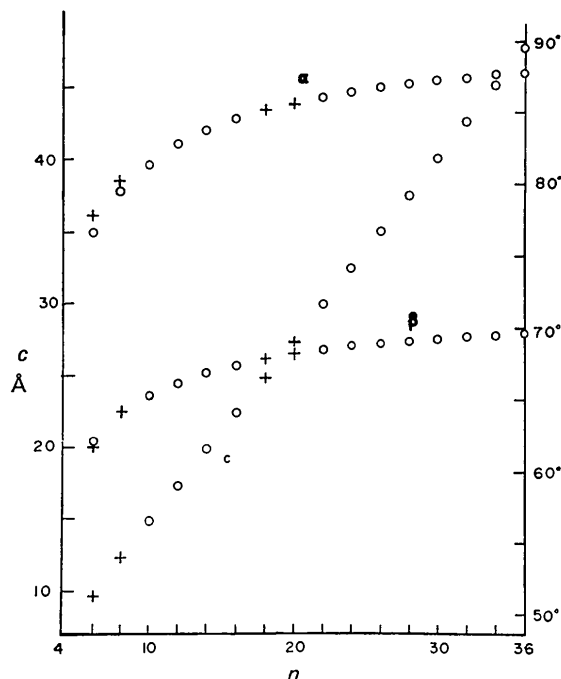


Fig. 2. Prediction (circles) c , α and β for n -even alkanes from the known cell for $C_{18}H_{38}$ (Nyburg & Lüth, 1972). Crosses are known experimental values.

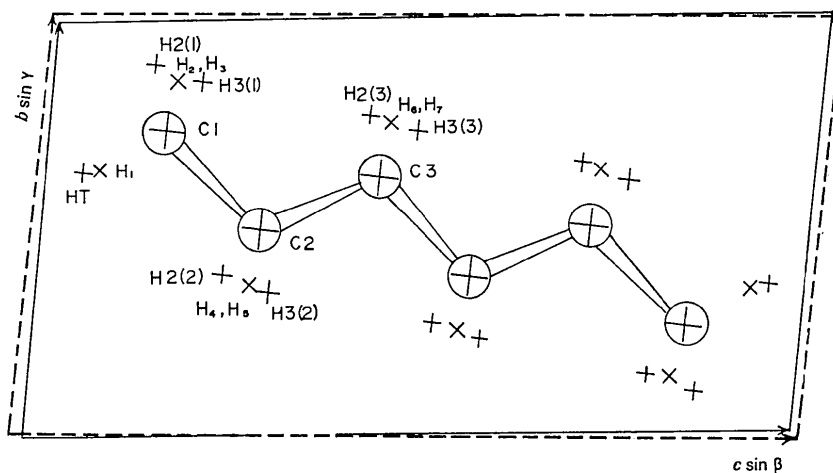


Fig. 3. Actual (Norman & Mathisen, 1961a) and predicted structure (x projection) for C_6H_{14} . The predicted cell is drawn with broken lines. The actual carbon positions are indicated by circles, the calculated positions by +. The 'averaged' hydrogen positions given by N & M are indicated by X, individual predicted positions by +.

Thanks are due to Dr A. E. Smith for the use of certain unpublished data and for financial support from the National Research Council of Canada and the Esso Research and Engineering Company.

References

- BROADHURST, M. G. (1962). *J. Res. Nat. Bur. Stds.* **66A**, 241–8.
 CRISSMAN, J. M., PASSAGLIA, E., EBY, K. Y. & COLSON, J. P. (1970). *J. Appl. Cryst.* **3**, 194–5.
International Tables for X-ray Crystallography (1952). Vol. I, p. 532. Birmingham: Kynoch Press.
 MATHISEN, H., NORMAN, N. & PEDERSEN, B. F. (1967). *Acta Chem. Scand.* **21**, 127–135.

- MÜLLER, A. & LONSDALE, K. (1948). *Acta Cryst.* **1**, 129–131.
 NORMAN, N. & MATHISEN, H. (1960). *Acta Cryst.* **13**, 1043.
 NORMAN, N. & MATHISEN, H. (1961a). *Acta Chem. Scand.* **15**, 1755–60.
 NORMAN, N. & MATHISEN, H. (1961b). *Acta Chem. Scand.* **15**, 1747–54.
 NYBURG, S. C. & LÜTH, H. (1972). *Acta Cryst.* **B28**, 2992–2995.
 SHEARER, H. M. M. & VAND, V. (1956). *Acta Cryst.* **9**, 379–384.
 SMITH, A. E. (1953). *J. Chem. Phys.* **21**, 2229–31.
 SMITH, A. E. (1972). Private communication.
 TEARE, P. W. (1959). *Acta Cryst.* **12**, 294–300.
 WYCKOFF, R. W. G. (1966). *Crystal Structures*. Vol. 5, p. 590. New York: Wiley-Interscience.

Acta Cryst. (1973). **B29**, 352

Structure Cristalline du Sulfure d'Erbium-Gallium, Er₃GaS₆

PAR S. JAULMES ET P. LARUELLE

Laboratoire de Physique de la Faculté de Pharmacie de Paris, 4 Avenue de l'Observatoire, 75006-Paris, France

(Reçu le 10 octobre 1972, accepté le 20 octobre 1972)

Er₃GaS₆ is orthorhombic, space group *Cmc*2₁, with cell constants $a=10.36$, $b=13.12$, $c=6.40$ Å and $Z=4$. The crystal structure has been determined from integrated Weissenberg data using Patterson and Fourier syntheses and refined by a least-squares method. The final R value is 0.079 for 506 reflexions. The erbium atoms have a sevenfold coordination.

Introduction

Lors de l'étude des systèmes L₂S₃-Ga₂S₃ (L=lanthanide+Y) trois séries de composés définis ont été mises en évidence.

— La première, de composition L_{10/3}Ga₆S₁₄, existe pour le lanthane et le cérium. Ces composés sont quadratiques et se rattachent à la formule A₄B₂C₂X₁₄. Les sites B et C sont tétraédriques et ici la coordinence de A est toujours de 8 (Lozac'h, Guittard & Flahaut, 1972).

— La deuxième série a la composition L₆Ga_{10/3}S₁₄; elle existe du lanthane au terbium inclus et pour l'yttrium. Ces composés sont hexagonaux et se rattachent à la formule cristallographique L₆B₂C₂X₁₄ déjà connue (De Saint-Giniez, Laruelle & Flahaut, 1968). Des séries isotopes existent si le gallium est remplacé par de l'aluminium ou de l'indium et le soufre par du sélénium (Patrie & Guittard, 1969). Dans ces composés, le gallium occupe totalement le site C tétraédrique et partiellement le site B octaédrique avec trois liaisons courtes presque coplanaires et trois liaisons plus longues. La coordinence de l'élément L est de huit avec la huitième liaison L-X plus longue que les sept premières (Flahaut & Laruelle, 1970).

— La troisième série a la composition L₃GaS₆ pour L=Dy, Ho, Er et Y (Lozac'h, Jaulmes & Guittard,

1971). Cette nouvelle phase orthorhombique n'apparaît pas avec les sulfures des autres métaux du groupe du gallium: on ne l'observe ni avec l'aluminium, ni avec l'indium. On ne l'obtient pas, non plus, en remplaçant le soufre par du sélénium, ni avec les autres terres rares.

Avec les terres rares de numéro atomique plus élevé, des combinaisons ternaires soufrées sont obtenues avec l'aluminium (Guittard, 1972, communication personnelle) ou avec le gallium, mais elles ne sont plus isotopes. Dans ces derniers composés, la question des coordinences de l'aluminium ou du gallium d'une part, et de la terre rare associée d'autre part, est posée. Les dérivés de l'aluminium ont une structure encore inconnue et nous décrivons ici celle des composés L₃GaS₆.

Détermination de la maille

Un monocristal de Er₃GaS₆* a été étudié par la méthode de Weissenberg. La maille est orthorhombique avec les paramètres:

$$\begin{aligned} a &= 10,36 \pm 0,02 \text{ \AA} \\ b &= 13,12 \pm 0,01 \\ c &= 6,40 \pm 0,01 \end{aligned}$$

* Cristal préparé par Mademoiselle A. M. Lozac'h.