

## Structure of $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$ from X-ray Powder Diffraction Data

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(Received 29 October 1987; accepted 5 April 1988)

### Abstract

The crystal structure of monoclinic  $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$  has been solved from X-ray powder diffraction data. The cell dimensions, obtained by indexing methods, are  $a = 7.5834$  (9),  $b = 8.1568$  (11),  $c = 7.6541$  (8) Å,  $\beta = 102.975$  (9)°. The space group is  $C2/m$  with  $Z = 4$ . Initial positional parameters for the Ca, K and P atoms were obtained by solution of the Patterson map resulting from integrated intensities of 92 unambiguously indexed reflections. The remaining atoms were located by an interpretation of the Fourier difference map. The structure refinement was effected by the Rietveld method. The final indicators were  $R_F = 0.046$ ,  $R_B = 0.054$  and  $R_{wp} = 0.137$ . The three-dimensional structure is built up from  $\text{PO}_4$  tetrahedra and  $\text{CaO}_8$  (two water molecules and six O atoms belonging to the phosphate groups) and  $\text{KO}_8$  (eight atoms belonging to the phosphate groups) polyhedra.

### Introduction

In recent years, there has been an increase in structural investigations of solids using powder diffraction data. The revival of interest in powder diffraction is associated partly with improvements in instrumental resolution and more importantly with the significant developments which have occurred in the last 20 years at every stage of structural analysis: the indexing methods and figures of merit for selecting between possible solutions, the pattern-fitting procedures without reference to a structural model, and the advent of the Rietveld method for structure refinement (Rietveld, 1969). Moreover, several works introduced by Werner (see, for example, Berg & Werner, 1977; Werner, 1986) have shown that standard Patterson Fourier maps deduced from powder diffraction data, collected with a Guinier–Hägg camera, can be employed for the solution of a completely unknown structure and combined with the Rietveld profile refinement. Similar techniques have been used for the determination of crystal structures from powder diffraction data collected with conventional diffractometers (Rudolf & Clearfield, 1985; Louër & Louër, 1987), from powder synchrotron X-ray data (Attfield, Sleight & Cheetham, 1986; Lehmann, Christensen, Fjellvåg, Feidenhansl &

Nielsen, 1987) and from time-of-flight neutron data (Cheetham, David, Eddy, Jakeman, Johnson & Torardi, 1986). The examination of the recently reported powder pattern for the new microcrystalline phase  $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$  (Louër, Deneuve & Ouillon, 1987) suggests the possibility of a structure analysis. In the present work we describe the procedure used for the *ab-initio* determination of the unknown crystal structure of the hydrated potassium calcium phosphate,  $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$ , from powder X-ray diffraction data collected with a conventional diffractometer with strictly monochromatic radiation.

### Experimental considerations

The chemical analysis of powdered  $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$  obtained from Rhône Poulenc has been reported previously as well as the value of the experimental density:  $2.69$  (10)  $\text{g cm}^{-3}$  (Louër, Deneuve & Ouillon, 1987). The powder diffraction pattern was scanned in steps of  $0.02^\circ$  ( $2\theta$ ) and fixed-time counting (40 s) was employed. At the end of data collection the stability of the intensity of the incident beam was checked by recording the first lines of the pattern. Data were obtained by using a Siemens D500 powder diffraction system and the following experimental conditions:

(a) A stabilized generator, operating at 45 kV, 40 mA, with a copper target and  $6^\circ$  take-off angle. Strictly monochromatic  $K\alpha_1$  radiation ( $\lambda = 1.5405981$  Å) was selected by means of an incident-beam curved-crystal germanium monochromator with asymmetric focusing (short focal distance 124 mm, long focal distance 216 mm).

(b) A scintillation detector with pulse-height discrimination.

(c) A 200 mm goniometer radius and  $0.05^\circ$  receiving-slit aperture.

Throughout the experiment the ambient temperature was maintained at 296 (1) K.

The adjustment of the diffractometer was checked by using standard materials [ $\text{Pb}(\text{NO}_3)_2$ ,  $\text{ZnO}$ ] as reference samples. The divergence slits located in the incident beam were adjusted to ensure a complete illumination of the specimen surface at about  $12^\circ$  ( $2\theta$ ). The resolution of the diffractometer for these experimental

conditions, obtained from an annealed barium fluoride sample, can be seen from the curve giving the variation of FWHM versus  $2\theta$  (Fig. 1). A shallow minimum is observed at about  $40^\circ$  ( $2\theta$ ) and the minimum value of FWHM is  $0.065^\circ$  ( $2\theta$ ). Its value is doubled at  $130^\circ$  ( $2\theta$ ). Special care is required in specimen preparation; a completely random orientation of crystallites is essential in determining the true relative intensities. The potassium calcium phosphate appeared sensitive to preferred orientation effects. To obtain a better refinement of the structure, the sample was mixed with an equal volume of amorphous silica. Moreover, to minimize the orientation effects which occur when powdered samples are pressed, a side-loading method was used.

### Data analysis

#### Indexing

The indexing of the powder pattern is described elsewhere (Louër, Deneuve & Ouillon, 1987). A high accuracy in the diffraction line positions is necessary; the absolute error in the peak measurements was estimated to be lower than  $0.04^\circ$  ( $2\theta$ ). The successive dichotomy method (Louër & Louër, 1972; Louër & Vargas, 1982) was applied to the first 20 lines of the pattern. The solution proposed by the program *DICVOL* is monoclinic with the refined cell parameters  $a = 7.5834$  (9),  $b = 8.1568$  (11),  $c = 7.6541$  (8) Å,  $\beta = 102.975$  (9)°,  $V = 461.36$  Å<sup>3</sup>. The reliability of the unit cell and indexing is indicated by the figures of merit (de Wolff, 1968; Smith & Snyder, 1979),  $M_{20} = 19.2$  and  $F_{20} = 28.1$  (0.0123, 58), in which the systematic absences due to Bravais lattice type are not taken into account. At this stage, the quality of the data concerning the line positions can also be evaluated by the average absolute magnitude of the discrepancy between observed and calculated  $2\theta$  values, i.e.  $|\Delta 2\theta| = 0.0123^\circ$ . The calculated density for  $Z = 4$  is  $2.77$  g cm<sup>-3</sup>, which is in accordance with the measured value ( $2.69$  g cm<sup>-3</sup>). The proposed unit cell indexes all the observed lines of the diffraction pattern.

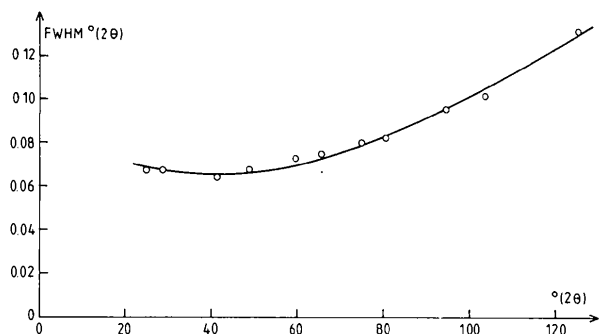


Fig. 1. Resolution curve of the diffractometer (annealed BaF<sub>2</sub> sample).

From the list of the unambiguous peaks detected in the powder pattern it was seen that all lines could be indexed using the restriction  $h + k = 2n$ . The possible space groups are *C2*, *Cm* and *C2/m*. Since the *C2* and *Cm* space groups, involving more variable parameters, did not improve the results, the structure was solved in the centrosymmetric *C2/m* space group.

#### Structure solution and refinement

The entire diffraction pattern was decomposed into its Bragg reflections without the use of structural information. The total pattern decomposition method of Sonneveld & Visser (1975), recently modified (Langford, Louër, Sonneveld & Visser, 1986), was applied. In the present analysis a pseudo-Voigt function, selected for representing the shape of the diffraction lines, was fitted to the raw experimental data. After a careful examination of the output list, 92 integrated intensities with unambiguous index assignments were obtained. This included approximately 40 weak reflections for which the intensity was evaluated from comparison with adjoining diffraction lines. After correction for Lorentz-polarization and multiplicity factors, these intensities were used as input data for the Enraf-Nonius *Structure Determination Package* (Frenz, 1978). Calculations were performed on a PDP 11/60 computer. The positions of the Ca, K and P atoms were derived from the calculation of a three-dimensional Patterson function. A least-squares refinement of these positions resulted in a conventional *R* value of 0.26. All the remaining atoms were found from a Fourier difference map. The refinement of the positions of the seven independent atoms, calculated from the 92 integrated intensities, gave an *R* value of 0.14.

At this stage, the least-squares structures refinement was continued with the Rietveld profile refinement method (Rietveld, 1969), by means of the computer program *DBW2.9* (Wiles & Young, 1981), locally modified for *R<sub>B</sub>*- and *R<sub>F</sub>*-factor calculations, which are the most significant indicators of the agreement between the structural model and the actual structure. The intermediate Lorentzian function was used for the representation of the individual reflection profiles. In order to describe the angular dependence of the peak full-width at half-maximum, the quadratic form in  $\tan\theta$  was used:

$$\text{FWHM}^2 = U \tan^2\theta + V \tan\theta + W,$$

where *U*, *V* and *W* are parameters whose values were refined. Values for background intensity were evaluated in regions where Bragg reflections have no contribution, and linear interpolation of these values led to the background correction. Integral intensities were distributed over three FWHM on either side of a diffraction line profile. The profile analysis refinement involved the

following parameters: 13 atomic coordinates, seven isotropic temperature factors, one scale factor, one zero-point parameter, four cell parameters, one asymmetry and three half-width parameters. In order to adjust the peak positions and the fit between the analytical profile shape and the observed line profiles, cell and instrumental parameters were allowed to vary from time to time during the refinement process. The refinement converged to  $R_F = 0.052$ ,  $R_B = 0.062$  and  $R_{wp} = 0.143$ . At this stage the last variable to refine was the preferred-orientation factor, which is included in the *DWB2.9* program and was discussed by Young & Wiles (1981). In this refinement the preferred-orientation parameter  $p$  was 0.08. Crystallographic details are given in Table 1, final atomic parameters in Table 2 and selected bond lengths and angles in Table 3. Fig. 2 shows graphically the fit obtained between calculated and observed patterns.\* This fit corresponds to satisfactory crystal structure model indicators ( $R_F = 0.046$ ,  $R_B = 0.054$ ) and to a profile factor of  $R_{wp} = 0.137$ .

### Results and discussion

The three-dimensional crystal structure of  $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$  is shown in stereoscopic view in Fig. 3. This figure, in which Ca—O and K—O bonds have been omitted for clarity, shows that the  $\text{H}_2\text{O}$  molecules are approximately located in planes parallel to  $(\bar{1}11)$  and intercalated between planes containing the phosphate groups. A projection of the structure on the (101) plane is given in Fig. 4(a), as well as partial projections along [001] (Figs. 4b and 4c). The Ca and K atoms are eight-coordinated. The Ca atom is surrounded by two water molecules and six O atoms belonging to four

\* Lists of bond lengths and bond angles, and observed and calculated data points corresponding to Fig. 2 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44890 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Details of Rietveld full-profile refinement*

Space group	C2/m
Z	4
2 $\theta$ range ( $^\circ$ )	12–91
Step-scan increment	0.02
No. of reflections	222
No. of structural parameters	20
No. of profile parameters	8
No. of atoms	7
$R_F = \sum  I_o^{1/2} - I_c^{1/2}  / \sum I_o^{1/2}$	0.046
$R_B = \sum  I_o - I_c  / \sum I_o$	0.054
$R_{wp} = \sum w_i [y_i(\text{obs.}) - y_i(\text{cal.})/c]^2 / \sum w_i [y_i(\text{obs.})]^2$	0.137
'Expected' $R_{wp}$	0.103

Table 2. *Positional and thermal parameters for  $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$*

	x	y	z	$B(\text{\AA}^2)$
Ca	0	0.7371 (2)	0	2.36 (3)
K	0	0.2229 (2)	0.5	2.44 (4)
P	0.2207 (3)	0	0.2506 (3)	2.50 (4)
O(1)	0.2879 (3)	0.1603 (2)	0.1751 (3)	2.13 (6)
O(2)	0.2813 (4)	0	0.4668 (5)	2.61 (10)
O(3)	0.0070 (4)	0	0.1905 (4)	2.63 (9)
$\text{H}_2\text{O}$	0.1545 (4)	0.5	0.1812 (4)	1.44 (8)

Table 3. *Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ )*

Ca—O distance			
Ca—O(1 <sup>ii,iii</sup> )	2.439 (2) (x2)	Ca—O(3 <sup>vi,vii</sup> )	2.587 (2) (x2)
O(1 <sup>iv,v</sup> )	2.397 (2) (x2)	$\text{H}_2\text{O}(1iv,iii)$	2.511 (2) (x2)
K—O distances			
K—O(1 <sup>ix,x</sup> )	2.808 (2) (x2)	K—O(2 <sup>iv,xii</sup> )	2.781 (2) (x2)
O(2 <sup>ix</sup> )	2.857 (2) (x2)	O(3 <sup>ix</sup> )	2.996 (3) (x2)
$\text{PO}_4$ group			
P—O(1 <sup>ix,iii</sup> )	1.561 (3) (x2)	O(1)—P—O(2)	113.8 (2)
O(2)	1.615 (4)	O(1)—P—O(1)	109.8 (1) (x2)
O(3)	1.582 (4)	O(1)—P—O(3)	106.9 (1) (x2)
		O(2)—P—O(3)	109.6 (2)
Possible hydrogen bonds			
$\text{H}_2\text{O}$ —O(2 <sup>xii</sup> )	2.628 (5)	O(2)— $\text{H}_2\text{O}$ —O(3)	91.1 (1)
O(3 <sup>xiv</sup> )	2.658 (5)		

Symmetry code: (i)  $x, y, z$ ; (ii)  $x, 1-y, z$ ; (iii)  $-x, 1-y, -z$ ; (iv)  $x - \frac{1}{2}, \frac{1}{2} + y, z$ ; (v)  $\frac{1}{2} - x, \frac{1}{2} + y, -z$ ; (vi)  $x, 1 + y, z$ ; (vii)  $-x, 1 + y, -z$ ; (viii)  $-x, y, -z$ ; (ix)  $x - \frac{1}{2}, \frac{1}{2} - y, z$ ; (x)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (xi)  $-x, y, 1 - z$ ; (xii)  $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$ ; (xiii)  $x, -y, z$ ; (xiv)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ .

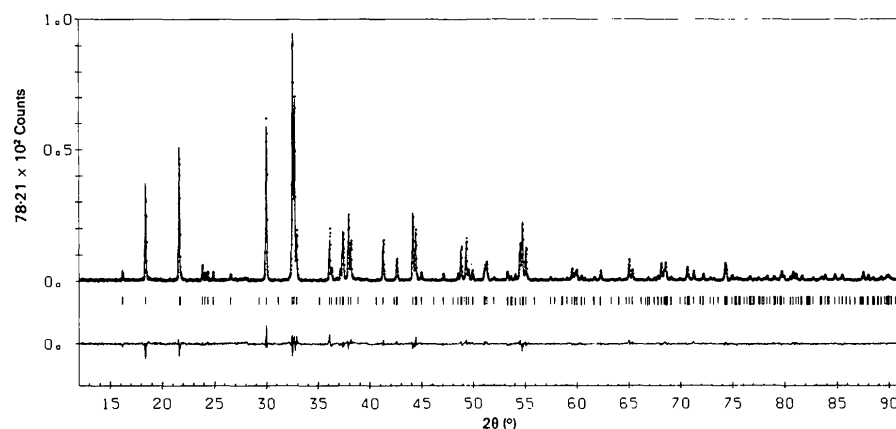


Fig. 2. The final Rietveld difference plot of  $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$ . In the upper portion, the observed data are shown by the dots; the calculated pattern is shown by the solid line. The lower portion is a plot of the difference, observed minus calculated.

phosphate groups. The distances Ca—O vary from 2.397 (2) to 2.587 (2) Å. The K atom is bonded to eight O atoms belonging to four bidentate PO<sub>4</sub> groups. The bond lengths range from 2.781 (2) to 2.996 (3) Å. The P atom and two vertices [O(2) and O(3)] of the phosphate group lie on a mirror plane at the coordinates  $y = 0$  (striped tetrahedra) and  $y = 0.5$  (non-striped tetrahedra); O(2) is bonded to four K atoms and O(3) to two Ca and two K atoms; the two other vertices [O(1)] located on both sides of the mirror plane are bonded to two Ca atoms and one K atom. The bond distances and angles of the phosphate group (Table 3) are in accordance with those generally observed in PO<sub>4</sub> ions (Baur, 1974). The water molecule also located on the mirror plane is bonded to two Ca atoms. It probably shares hydrogen bonds with O(2) and O(3), since the distances H<sub>2</sub>O—O(2) and H<sub>2</sub>O—O(3) and the angle O(2)—H<sub>2</sub>O—O(3) (Table 3) are compatible with the criteria required for such bonds (Baur & Khan, 1970) and with the geometry of the environment of H<sub>2</sub>O molecules in hydrated salts (Ferraris & Franchini-Angela, 1972).

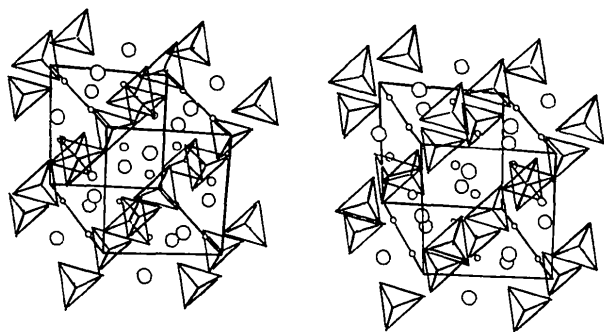


Fig. 3. Stereoscopic ORTEP (Johnson, 1965) view of KCaPO<sub>4</sub>·H<sub>2</sub>O (CaO and KO bonds are omitted for clarity) along  $b$ , with  $a$  horizontal and  $c$  vertical: small circles, Ca; medium circles, K; and large circles, H<sub>2</sub>O.

These results demonstrate that the structure of KCaPO<sub>4</sub>·H<sub>2</sub>O consists of an infinite network of CaO<sub>8</sub> and KO<sub>8</sub> polyhedra and PO<sub>4</sub> tetrahedra. Fig. 4(a) shows that the edge-sharing CaO<sub>8</sub> and KO<sub>8</sub> polyhedra are connected together by the PO<sub>4</sub> tetrahedra with which they alternately share an edge (CaO<sub>8</sub>) and a vertex (KO<sub>8</sub>). In the direction parallel to [010], the CaO<sub>8</sub> polyhedra (Fig. 4b) share an edge formed alternatively by two water molecules and two O atoms of PO<sub>4</sub> groups, whereas the KO<sub>8</sub> polyhedra (Fig. 4c) are joined together by face and edge sharing.

To conclude, the solution of the crystal structure described in this work was made possible because special attention was paid to the data quality required at every stage of the structure analysis: accuracy of angular positions of diffraction lines for indexing as well as high resolution for indexing, extraction of Bragg components and evaluation of the background level, which is of importance in Rietveld refinements. In spite of the limited amount of data typically encountered in a powder diffraction pattern, this example of moderate complexity shows that, under favorable circumstances, an *ab-initio* structure determination can be performed from data collected by means of a conventional diffractometer with optimum resolution obtained by monochromatic radiation.

The authors thank Dr F. Deneuve, Rhône Poulenc Recherches, for her cooperation, and Professor P.-E. Werner for his many valuable suggestions.

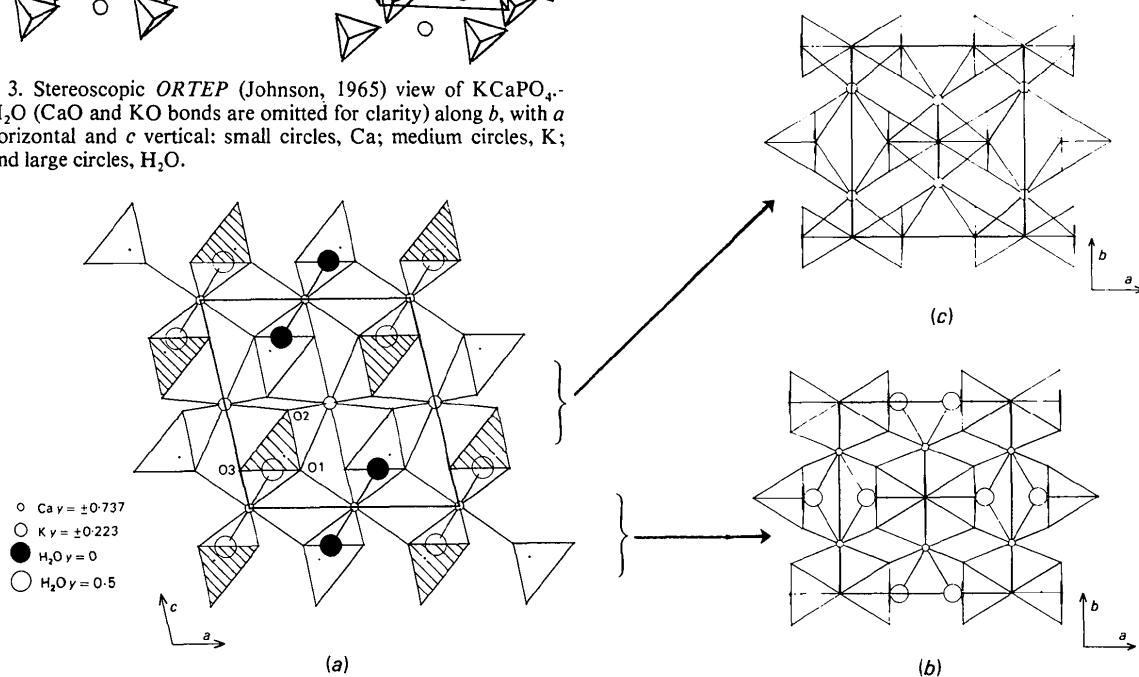


Fig. 4. Projection of the crystal structure on (101) plane (a) and partial projections along [101] of the Ca environment (b) and the K environment (c).

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*Acta Cryst.* (1988). **B44**, 467–474

## Electron Diffraction Observations from Some So-Called ‘LnMS<sub>3</sub>’ Layer Compounds Isostructural with ‘~LaCrS<sub>3</sub>’ and from Cannizzarite, ~Pb<sub>46</sub>Bi<sub>54</sub>S<sub>127</sub>

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(Received 29 March 1988; accepted 23 May 1988)

### Abstract

Electron diffraction data are reported and discussed for a series of so-called ‘LnMS<sub>3</sub>’ compounds (Ln = La, Ce, Pr and Nd, M = Cr; Ln = La, M = Ti, V and Cr) and for cannizzarite (~46PbS.27Bi<sub>2</sub>S<sub>3</sub>). The structures of all these compounds consist of two layer types alternating along the stacking direction – which is the zone axis in most instances. In the first group the mismatch between the layers varies slightly (by up to 2.5%) as the cations are varied. In the last we find only the ~12/7 and 17/10 layer matches, and not their combinations 46/27 and 41/24 as reported by Matzat [*Acta Cryst.* (1979), **B35**, 133–136].

### Introduction

There is a group of synthetic and mineral sulfosalts with apparently complex structures and large unit cells which can be simply described as consisting of stacks of two alternating layer types, *A* and *B*. One is a thin tetragonal [= (100)] section of NaCl type, the other a thin trigonal [= (111)] section of NaCl type. The complexity arises mainly from the incommensurability between their unit-layer vectors, but also from the

consequent small distortions (modulation) of the layers. Many examples of such cases of two interpenetrating substructures have been reviewed and described in some detail (Makovicky & Hyde, 1981) ranging from the most complex, such as cylindrite (~FePb<sub>3</sub>Sn<sub>4</sub>-Sb<sub>2</sub>S<sub>14</sub>) and the related franckeites (~FePb<sub>6-x</sub>Sn<sub>2+x</sub>-Sb<sub>2</sub>S<sub>14</sub>) and lengenbachite [~Pb<sub>6</sub>(Ag,Cu)<sub>2</sub>As<sub>4</sub>S<sub>13</sub>] to the simplest such as ‘~LaCrS<sub>3</sub>’ and other ‘~LnMS<sub>3</sub>’ (Ln = a rare-earth or yttrium cation). Their structural details are best explored by electron microscopy/diffraction (Williams & Hyde, 1988; Williams & Pring, in preparation). A previous paper (Otero-Diaz, Fitz Gerald, Williams & Hyde, 1985) included such an examination of ‘~LaCrS<sub>3</sub>’; the purpose of the present paper is a similar examination, first of other ‘~LnMS<sub>3</sub>’ and then of cannizzarite (~Pb<sub>46</sub>Bi<sub>54</sub>S<sub>127</sub>).

### ‘~LnMS<sub>3</sub>’

This group of structurally similar compounds is a particularly simple example of non-commensurate layer structures in which the pseudotetragonal layer *T* is two atom layers thick and the pseudo(ortho)hexagonal layer *O* is three atoms thick. Fig. 1 shows the monoclinic structure of ‘~LaCrS<sub>3</sub>’ as reported by Kato, Kawada & Takahashi (1977) which has  $a = 5.936$ ,  $b = 5.752$ ,  $c = 11.036$  Å,  $\alpha = 90.39$ ,  $\beta = 95.30$  and  $\gamma = 90.02^\circ$

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