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Structural Study of Three Modulated Phases in Rb_2ZnBr_4

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Abstract

The crystal structures of Rb_2ZnBr_4 at 293, 140 and 95 K have been studied using single-crystal X-ray diffraction or single-crystal neutron diffraction (for the structure at 95 K). The so-called incommensurate structure (293 K) and the two threefold superstructures (140 and 95 K) have been determined using a computer program for modulated structures. The resulting 293 K structure has space group $Pcmn(00\gamma)(ss\bar{1})$. Because of conflicting symmetry evidence in the literature, several other space groups were tried, but they yielded less satisfactory results. For the other two phases, the space group $Pc2_1n$ was used. The R values are 0·08 (for 1512 main and 2654 satellite reflections), 0·12 (1494 + 3002 reflections) and 0·05 (for 502 + 980 reflections) for the structures at 293, 140 and 95 K respectively. There is no clear structural difference between the two threefold superstructure phases. The displacive modulation is strikingly similar in the three structures. It mainly consists of rotations of the rather rigid $ZnBr_4$ tetrahedra. The amplitude of the modulation functions is roughly 35% smaller in the 293 K structure than in the 95 K structure. The modulation functions of the two threefold superstructures show a strong pseudo-$Pcmn(00\gamma)(ss\bar{1})$ symmetry. The temperature parameters clearly reveal that librations of the tetrahedra form an important component of the thermal vibrations. Crystal data at 95 (1) K: $M_r = 555{\cdot}9$, $a = 13{\cdot}184$ (4), $b = 7{\cdot}599$ (2), $c = 9{\cdot}623$ (5) Å, $V = 964{\cdot}1$ Å^3.

1. Introduction

In Rb_2ZnBr_4 five phase transformations are observed at atmospheric pressure, at temperatures $T_i = 374$, $T_c = 190$, $T_3 = 112$, $T_4 = 77$ and $T_5 = 50$ K [see, for example, Yamaguchi, Sawada, Takashige & Nakamura (1982) and Nomoto, Atake, Chaudhuri & Chihara (1983)]. The values found in the literature for these temperatures scatter around the above-mentioned values. Rb_2ZnBr_4 melts at 753 K (Sawada, Shiroishi, Yamamoto, Takashige & Matsuo, 1977). The six solid phases are denoted as N (normal), I (incommensurate), F (ferroelectric), IV, V and VI from high to low temperatures. T_c has a hysteresis of about 10 K. This value strongly depends on the sample: de Pater (1978) observed that part of a crystal remained in phase I even at 4 K, and de Boer (1984) observed that a crystal remained in phase I at temperatures below 100 K. No hysteresis has been observed for the other phase transitions.

In phase N (above T_i) Rb_2ZnBr_4 has the β-K_2SO_4-type structure with unit-cell dimensions $a = 13{\cdot}386$ (3), $b = 7{\cdot}679$ (2) and $c = 9{\cdot}753$ (2) Å at 373 K (de Pater, 1979). In phase I (between T_i and T_c) the crystal structure is modulated by a displacive modulation wave with the modulation wave vector parallel to $\mathbf{c}^*$: $\mathbf{q} = \gamma\mathbf{c}^*$. The value of γ is constant at 5/17 (0·294) within experimental error in the large temperature interval between T_i and $T_c + 10$ K [see de Pater (1979) and Iizumi & Gesi (1983)]. Thus, in this range the structure of the so-called incommensurate phase is commensurate (Hogervorst & de Wolff, 1982).

Below the 'lock-in' phase-transition temperature T_c the value of γ is 1/3, and hence phase F has a threefold superstructure. It is not yet clear what happens between $T_c + 10$ K and T_c. Until recently it has been assumed that on lowering the temperature from $T_c + 10$ K, γ increases monotonically from 0·294 to about 0·31 at T_c, where it jumps to 1/3. Recent measurements of Iizumi & Gesi (1983), however, indicate a more complex behaviour. These measurements suggest that several extra phase transitions exist in that small temperature

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region, γ jumping at each transition temperature to a new value.

The symmetry of the threefold superstructure in phase F (between T_c and T_3) is $Pc2_1n$ according to de Pater (1979) and Ueda, Ikeda & Terauchi (1982). Little is known about the structure of phases IV, V and VI. According to Ueda *et al.* (1982) these structures have the same threefold unit cell as phase F. They observed that phase IV shows the same systematically absent X-ray reflections as phase F, corresponding to a c glide normal to **a** and an n glide normal to **c**. In phases V and VI they only observed the n-glide plane. Yamaguchi *et al.* (1982) observed that the ferroelectricity along **b**, which appears on cooling at T_c (therefore often called the Curie temperature), is present in all phases below this temperature. In phase IV alone, they also observed a double D–E hysteresis loop along the **a** axis. This indicates that this phase is antiferroelectric along **a**.

Magnetic resonance measurements on Rb_2ZnBr_4 (Belobrova, Aleksandrova & Moskalev, 1981) show three ^{81}Br NQR frequencies in phase N, 12 in phase F and 32 in phase IV. In phase N the intensity of one of the three frequencies is twice as large as that of the other two. For phase N and phase F these results correspond to the symmetry information mentioned above. The number of lines in phase IV, however, does not correspond to a threefold superstructure with symmetry $Pc2_1/n$. The frequency peaks of phase IV do not have a normal shape and Belobrova *et al.* suggest that either several of the observed peaks are close doublets or the structure is incommensurate.

De Pater (1979) determined the structure of Rb_2ZnBr_4 in phase N at 373 K from a neutron diffraction powder diagram. He used the same technique to determine the average structure at 300 K (phase I) and at 4 K (phase VI). In all cases he fitted the measurements to a structure model with the unit-cell size and symmetry of phase N. He used split atoms to account for the thermal motion at 373 K and for the modulation displacements in the other cases.

De Jager (1980) determined the structure of Rb_2ZnBr_4 at 300 K in a threefold superstructure approximation, using 730 X-ray reflections, of which 78 are satellites. His structure model has the same unit-cell size and symmetry as the structure of phase F: a threefold supercell and space group $Pc2_1n$.

Several other compounds exist the crystals of which have the phase sequence normal – incommensurate – threefold superstructure. The phase-transition temperatures T_i and T_c are 553 and 403 K for K_2ZnCl_4 (Gesi & Iizumi, 1979), 303 and 194 K for Rb_2ZnCl_4 (Quilichini & Pannetier, 1983), and 129 and 94 K for K_2SeO_4 (Iizumi, Axe, Shirane & Shimaoka, 1977). In addition, many other A_2BX_4 compounds show incommensurately and commensurately modulated structures related to the modulated structure of Rb_2ZnBr_4 (Hogervorst, 1986).

In this paper structure determinations of Rb_2ZnBr_4 at 293, 140 and 95 K are presented. At these temperatures Rb_2ZnBr_4 is in phase I, phase F and phase IV respectively.

2. Experimental

Transparent single crystals of Rb_2ZnBr_4 were grown from an aqueous solution containing RbBr and $ZnBr_2$ in the molar ratio 2:1 (RbBr: 99·9%, Alpha Products; $ZnBr_2$: 99·8%, Ventron GmbH). At room temperature, another compound (unidentified) crystallizes first from the fresh solution. The molar ratio of the two components in the solution then changes. Finally, clear Rb_2ZnBr_4 crystals appear.

Attempts to make small spheres (diameter <0·3 mm) of Rb_2ZnBr_4 failed. Therefore, the X-ray measurements were performed on small ellipsoid-shaped crystals. Because of the strong absorption of X-rays in Rb_2ZnBr_4 (the linear absorption coefficient of Mo $K\alpha$ radiation in Rb_2ZnBr_4 is 28·2 mm^{-1}), special care was necessary for the absorption correction (for details see §4).

Experimental details of the diffraction measurements at the three temperatures are given in Table 1. The X-ray measurements were performed with an Enraf–Nonius CAD-4 four-circle diffractometer. During the measurements at 140 K the crystal was cooled by a controlled flow of N_2 gas. The neutron diffraction measurements were carried out with the four-circle diffractometer at the HFR reactor in Petten. The crystal was mounted in an He-flow cryostat (Herbert & Campbell, 1977).

At the three temperatures the main reflections and the first-order satellites were measured in one octant. No higher-order satellites were measured because they are not visible on precession photographs. Each reflection was measured until the desired accuracy [$\sigma(I) \leq 0{\cdot}02I$] or the maximum measuring time was reached. In the neutron diffraction measurements the measurement of a reflection was stopped after 900 s if the intensity was very low [$I \leq \sigma(I)$]. For negative measured intensities I was set to zero. All these weak reflections, however, are included in the data set. Lorentz–polarization corrections of the X-ray measurements were applied according to Azaroff (1955). No extinction correction was used.

During the refinements of the structures at room temperature and 140 K, a few reflections were removed from the data set (see Table 1). Those reflections suspected of extinction have small θ, a very high intensity and a calculated structure factor which is much higher than the observed one. Those reflections with $\lambda/2$ contamination have a low intensity, a calculated structure factor which is much lower than the observed one and a very strong reflection at the position with double indices. It has been checked that

Table 1. *Data on the structure determinations of* Rb_2ZnBr_4

Temperature (K)	293 (2)	140 (3)	95 (1)
Stability (K)	±5	±3	±0·2
Radiation	Mo $K\alpha$, 0·7107 Å	Mo $K\alpha$, 0·7107 Å	Neutrons, 1·304 Å
Monochromator	Graphite	Graphite	Double Cu(220)
Crystal shape	Ellipsoid	Ellipsoid	Rough sphere
Diameter (mm)	0·21–0·27	0·23–0·28	3·5
Max. measurement time (s)	600	180	1800
No. of reflections used for cell constants	†	25	13
θ range for cell constants (°)	†	12–14	20–63
Max. θ (°)	30	30	38·3
hkl range *h*	0–18	0–18	0–12
k	0–10	0–10	0–7
l	0–13	0–13	0–9
Space group	$Pcmn\,(00\gamma)(ss\bar{1})$	$Pc2_1n$	$Pc2_1n$
a (Å)	13·330 (3)†	13·198 (5)‡	13·184 (4)
b (Å)	7·656 (2)†	7·594 (4)‡	7·599 (2)
c (Å)	9·707 (2)†	3×9·614 (3)‡	3×9·623 (5)
$\gamma(\mathbf{q} = \gamma\mathbf{c}^*)$	0·293§	$\frac{1}{3}$	$\frac{1}{3}$
No. of reflections			
Main	1512	1494	502
Satellite	2654	3002	980
Total	4166	4496	1482
Reflections removed			
Extinction	0200, 0400, 1030, 4000	1030	—
$\lambda/2$ contamination	2000, 1100	2000, 1100	—
Weighting scheme	$1/\sigma^2(F_o)$	$1/[\sigma^2(F_o)+(0{\cdot}05F_o)^2]$	$1/\sigma^2(F_o)$
No. of parameters			
Basic structure position	13	20	20
Modulation Fourier coefficient	16	42	42
Temperature	26	42	42
Scale factor	1	1	1
Total	56	105	105
Largest shift in last refinement cycle	0·012σ	0·17σ	0·21σ
wR (all reflections)	0·080	0·119	0·050
wR (main reflections)	0·063	0·088	0·040
wR (satellite reflections)	0·167	0·154	0·073
D (Å)¶	0·037	0·047	0·025

† Cell constants taken from de Pater (1979).

‡ These lattice parameters have larger errors than the e.s.d.'s indicate, because of the strong absorption.

§ Taken from Iizumi & Gesi (1983).

¶ *D* is defined in equation (3).

the $\lambda/2$ contamination is indeed of the proper magnitude to explain these discrepancies.[*]

The atomic scattering factors and the dispersion corrections of Rb^+, Zn^{2+} and Br^- for Mo $K\alpha$ radiation were taken from *International Tables for X-ray Crystallography* (1974). The neutron diffraction scattering amplitudes of Rb, Zn and Br, 7·08, 5·680 and 6·79 fm respectively, were taken from Koester & Yelon (1982).

3. Symmetry

A full treatment of the symmetry of incommensurately modulated crystal structures has been given by de Wolff, Janssen & Janner (1981). For typographical reasons the notation of the four-dimensional space groups used in this paper differs from that of de Wolff *et al.* In our notation, for example, the space-group symbol

$$Pcmn(00\gamma)(ss\bar{1}) \qquad (1)$$

gives the (standard) three-dimensional space group of the basic structure (*Pcmn*), the direction and length of the modulation wavevector $(0\mathbf{a}^* + 0\mathbf{b}^* + \gamma\mathbf{c}^*)$ and the way the symmetry operations act on the modulation functions (*s*: shift of half the modulation wave length; $\bar{1}$: inversion) respectively. The individual symmetry operations are denoted as $c(s)$, $m(s)$, $n(\bar{1})$, *etc.*

Table 2. *Reflection conditions observed at* 293 K

(i) $0klm$: $l+m$ = even $\rightarrow c(s)$
(ii) $h0lm$: m = even $\rightarrow m(s)$
(iii) $hk00$: $h+k$ = even $\rightarrow n(\bar{1})$

Although the room-temperature phase of Rb_2ZnBr_4 is a commensurate superstructure [$\gamma = 5/17$, *cf.* Hogervorst & de Wolff (1982)], it shows systematic extinctions which strongly suggest a (3 + 1)-dimensional space group as the best description of its symmetry. The reflection conditions which we observed on X-ray precession photographs are shown in Table 2. In our diffractometer results, these rules are obeyed as well. Since the three symmetry operations listed in Table 2 generate the complete group $Pcmn(00\gamma)(ss\bar{1})$, it can be expected that this symmetry will lead to a satisfactory description of the structure. It has indeed turned out to be the best basis for refinement.

The true symmetry of the superstructure has not been solved, in spite of considerable effort. For $\gamma = 5/17$, only the elements $c(s)$ and $n(\bar{1})$ in the above symbol correspond to three-dimensional elements, *viz.* *c* and *n*, in the required unit cell with $c_s = 17c$. The element $m(s)$ is lost. This can be seen, for example, from the reflection condition (ii) which for the multiple cell $(L = 17l + 5m)$ does not lead to a parity condition on *L* in *h0L*. Accordingly, the true space group would become $Pc2_1n$ in the multiple cell. This is in flagrant contradiction with two observations:

(*a*) Crystals grown from aqueous solution at about 300 K have a very pronounced 222 symmetry (de Pater, 1978; de Wolff, 1980). The same point group was also seen in experiments by Dam & Janner (1983). *With a true symmetry $Pc2_1n$, the point group would be* *m*2*m*, and *m*2*m* is not even a subgroup of 222.

(*b*) Neutron diffraction experiments of Iizumi & Gesi (1983) show that reflections 0210, 0201 and $022\bar{1}$ have intensities differing significantly from zero at 298 K. These reflections are not allowed by condition (i) (see Table 2), so they exclude the presence of a *c*-glide plane in the actual superstructure. It should be remarked, however, that their intensities are very small indeed. Therefore, it must be concluded that the structure almost has symmetry $Pcmn(00\gamma)(ss\bar{1})$. [The choice of *a*

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[*] Lists of observed and calculated structure factors at 293, 140 and 95 K have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44555 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and b axes was not stated by Iizumi & Gesi. Judging from other reflection intensities we concluded that their a (b) is our b (a), so in the indices mentioned above h and k have been interchanged with respect to those given in their paper.] The two observations together suggest that the actual space group is $P2_12_12_1(00\gamma)$-$(\bar{1}\bar{1}1)$.

Certain physical properties have been checked by other authors, mainly with a view to test a possible departure from centrosymmetry. All results, however, have been negative, so that no definite conclusion can be drawn:

(*a*) Smid (1984): no optical second harmonic generation (detection limit: 10^{-4} times the second harmonic generation level of quartz);

(*b*) Yamaguchi *et al.* (1982): no ferroelectricity or pyroelectricity.

A definite identification of the space group of Rb_2ZnBr_4 in the room-temperature phase cannot be made. Structure refinements have been performed in three space groups (§4). $Pcmn(00\gamma)(ss\bar{1})$ gives the best results. Hence, the room-temperature structure of Rb_2ZnBr_4 can at least to a good approximation be described by this space group.

The room-temperature structure will be treated as incommensurate in the structure refinements, notwithstanding its rational modulation wavevector. Table 3 gives the symmetry operations of space group $Pcmn(00\gamma)(ss\bar{1})$. The atoms on the mirror plane [$m(s)$] are at special positions. The modulation functions $d_1(t)$ and $d_3(t)$ of such atoms, describing the displacement components in the **a** and **c** directions (see §5), cannot contain odd harmonics. The modulation functions $d_2(t)$ of these atoms cannot contain even harmonics. These symmetry restrictions exist together with the usual ones on the basic structure positions and the temperature parameters.

No inconsistencies exist concerning the space group of phase F: $Pc2_1n$. Rb_2ZnBr_4 is ferroelectric along **b** in this phase (Yamaguchi *et al.*, 1982) and generates second harmonic light at a level of about 0·1 times that of quartz (Smid, 1984). The systematic absences for the c- and n-glide planes are clearly present (Ueda *et al.*, 1982). A few apparent violations of these systematic absences in our measurements were shown to be caused by $\lambda/2$ contamination.

The space group of phase IV is still a puzzle. Despite the fact that the observations of Yamaguchi *et al.* (1982) and Belobrova *et al.* (1981) indicate that the structure of this phase is different from that of phase F, we could not find differences in the diffraction symmetry: the systematic absences of the c- and n-glide planes are still present [as has also been found by Ueda *et al.* (1982)]: no extra reflections could be found on the $\mathbf{a}^*$, $\mathbf{b}^*$ or $\mathbf{c}^*$ axes; no tripling of **a** or **b** could be found; it has been checked that the modulation wavevector is $\mathbf{c}^*/3$, and not, for example $3\mathbf{c}^*/8$, as suggested by the results of the magnetic resonance measurements of Belobrova *et al.* (1981). Moreover, as in phase F, in this phase Rb_2ZnBr_4 is ferroelectric along **b** (Yamaguchi *et al.*, 1982) and generates second harmonic light (Smid, 1984). Therefore it is concluded that the structure of this phase can be described as a threefold superstructure with space group $Pc2_1n$, like phase F. This symmetry has been used for the structure determination.

Table 3. *Space-group operations of* $Pcmn(00\gamma)(ss\bar{1})$

R, s, ε and τ are given for each operation.

$$\begin{array}{llll}
c(s): \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \end{bmatrix}, & 1, \frac{1}{2} & \quad 2_1(\bar{1}): \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \end{bmatrix}, & -1, \frac{1}{2} \\
m(s): \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} 0 \\ \frac{1}{2} \\ 0 \end{bmatrix}, & 1, \frac{1}{2} & \quad 2_1(\bar{1}): \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \begin{bmatrix} 0 \\ \frac{1}{2} \\ 0 \end{bmatrix}, & -1, \frac{1}{2} \\
n(\bar{1}): \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{bmatrix}, & -1, 0 & \quad 2_1(1): \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{bmatrix}, & 1, 0 \\
\bar{1}(\bar{1}): \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, & -1, 0 & \quad 1(1): \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, & 1, 0
\end{array}$$

4. Absorption correction and refinement

The structures have been refined using the computer program described by Hogervorst (1986). In this program the crystal structure is explicitly described as an incommensurately or commensurately modulated structure, according to the formalism of de Wolff *et al.* (1981). To describe the atomic positions, average coordinates and Fourier coefficients of the modulation functions are used instead of individual coordinates. The threefold superstructures of Rb_2ZnBr_4 at 140 and 95 K could have been refined with a conventional program as well [see, for example, Vermin, Verschoor & IJdo (1976), or van Koningsveld (1983)], but using the program for modulated structures has certain advantages:

(*a*) direct comparison of incommensurately and commensurately modulated structures is possible;

(*b*) fewer temperature parameters are involved because the program automatically uses the same temperature parameters for all corresponding atoms in different subcells;

(*c*) the correlations between the parameters in the model are smaller in general, which gives better convergence.

In order to represent the threefold superstructures properly in the program, space group $Pc2_1n(00\gamma)(s\bar{1}\bar{1})$ has been used, with the symmetry operations given in Table 4.

For the 293 K structure, only the first harmonics are considered in the refinements, because the second- and higher-order satellites are very much weaker than the first-order ones (they were not seen by X-ray diffraction). For the two threefold superstructures, the second and higher harmonics do not exist.

Table 4. *Four-dimensional symmetry operations used to describe a threefold superstructure with space group $Pc2_1n$*

$$c(s):\ \begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix},\ \begin{bmatrix}\frac{1}{2}\\0\\\frac{1}{2}\end{bmatrix},\ 1,\tfrac{1}{2}\qquad 2_1(\bar{1}):\ \begin{bmatrix}-1&0&0\\0&1&0\\0&0&-1\end{bmatrix},\ \begin{bmatrix}0\\\frac{1}{2}\\0\end{bmatrix},\ -1,\tfrac{1}{3}$$

$$n(\bar{1}):\ \begin{bmatrix}1&0&0\\0&1&0\\0&0&-1\end{bmatrix},\ \begin{bmatrix}\frac{1}{2}\\\frac{1}{2}\\\frac{1}{2}\end{bmatrix},\ -1,-\tfrac{1}{6}\qquad 1(1):\ \begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix},\ \begin{bmatrix}0\\0\\0\end{bmatrix},\ 1,0$$

Table 5. *Comparison of refinements using reflections corrected for absorption with (A) and without (B) the anisotropic part*

N is the number of reflections used, *wR* is the residual and *D* is the average of the differences between the maximum and minimum of the distance types Zn–Br(*i*) [$i = 1,2,3,4$, see equation (3)]. Weighting scheme for refinements 1–6: $w_r = 1/\sigma^2(F_o)$; for refinements 7,8: $w_r = 1/[\sigma^2(F_o) + (0{\cdot}05F_o)^2]$.

	Temp.	Reflections		*A*		*B*	
No.	(K)	used	*N*	*wR*	*D*(Å)	*wR*	D(Å)
1	293	$I>10\sigma(I)$	528*	0·0640	0·051	0·0689	0·051
2	293	$h^2+k^2+l^2<100$	1678*	0·0771	0·038	0·0783	0·037
3	293	All	4166	0·0804	0·037	—	—
4	140	$I>10\sigma(I)$	890*	0·0657	0·067	0·0730	0·067
5	140	All	4498*	0·0771	0·052	0·0796	0·057
6	140	All	4496	0·0735	0·056	—	—
7	140	All	4498*	0·1206	0·047	0·1242	0·045
8	140	All	4496	0·1188	0·047	—	—

* Including two reflections which are strongly contaminated by $\lambda/2$.

All the refinements were based on structure factors. The residual (*wR*) was calculated using

$$wR = \textstyle\sum_r w_r(F_{or} - |F_{cr}|)^2/\sum_r w_r F_{or}^2, \tag{2}$$

in which the summations are over all used reflections, w_r is the weight of reflection *r*, F_{cr} is the calculated structure factor and F_{or} is the observed structure amplitude.

The linear absorption coefficient (μ) for Mo $K\alpha$ radiation in Rb_2ZnBr_4 is 28·2 mm^{-1}, that for neutrons ($\lambda = 1{\cdot}304$ Å) is 0·0082 mm^{-1}. For the neutron diffraction data no absorption correction is needed, but for the X-ray measurements a large correction is necessary. Because the absorption is very strong and because the crystals used for these measurements are not spheres, the usual isotropic correction (*International Tables for X-ray Crystallography*, 1959) is not sufficient. Therefore, the reflection intensities have been corrected with the computer program *CAMEL JOCKEY* of Flack (1974, 1975).

The absorption correction is derived by this program from a separate set of measurements, consisting of 17 non-equivalent reflections and their symmetry equivalents, each measured for $\psi = n \times 20°$ ($n = -4$, -3, -2, -1, 0, 1, 2, 3, 4; ψ is the rotation angle around the reflection vector), as far as the geometry of the diffractometer allowed. In total, 1227 of these measurements were performed at room temperature (some of them are double) and 1160 at 140 K. If the crystal had been a sphere, then for each of the 17 non-equivalent reflections all the measurements should have given the same intensity within experimental error. The program calculates the average for each of the 17 groups of intensities, and calculates the correction necessary to make the eight measurements at $\psi = 0°$ in each group equal to this average. This correction, which is a function of the diffractometer angles, is applied to the intensities in the main data set, together with the usual isotropic correction.

Because the crystals are not spheres, the choice of the radius (*R*) for the isotropic part of the absorption correction is ambiguous, as pointed out by Flack (1974). For both crystals used for the X-ray measurements, $\mu R = 3{\cdot}5$ was chosen. For the room-temperature measurements, $\mu R = 3{\cdot}8$ was also tried, in order to investigate the effect of a different choice of radius. Using 1678 reflections (those with $h^2+k^2+l^2<100$), refinements resulted in $wR = 0{\cdot}07713$ and 0·07719 for $\mu R = 3{\cdot}5$ and 3·8 respectively. In the case of $\mu R = 3{\cdot}8$, the diagonal temperature parameters were about 0·002 larger than in the case of $\mu R = 3{\cdot}5$, while the other parameters did not show noticeable differences. Therefore it can be concluded that the only effect of choosing a different radius is that the refinement leads to slightly different temperature parameters. For the crystal used for the room-temperature measurements, the program used four nonzero coefficients (including a scale factor) in the function that describes the transmission factor. The correction factors for the anisotropic part of the absorption correction applied to the intensities were between 0·77 and 1·18. For the studies at 140 K, nine nonzero coefficients were used, and the factors were between 0·72 and 1·35.

The effect of the absorption correction can be evaluated by comparing the results of refinements using reflections which are corrected as described, with the results of refinements using the same reflections corrected only by the isotropic part of the absorption correction. These results are shown in Table 5. It can be concluded from the residuals in this table that the absorption correction according to Flack is significantly better than the mere isotropic correction. The correction has a greater effect on the stronger reflections because the corrections are larger for stronger reflections. Besides the residual, another quantity is used to obtain information about the quality of the model. This quantity (*D*) is calculated from the Zn–Br distances within the rather rigid $ZnBr_4$ tetrahedra. The use of this quantity is based on the fact that all Zn–Br distances of a certain type [*e.g.* Zn–Br(1)] will, to a good approximation, be equal. This is true because the tetrahedra in different subcells have about the same surroundings since the deviation of the structure from the symmetry of the normal phase (*N*) is small. *D* is defined by

$$D = \tfrac{1}{4}\sum_{i=1}^{4} \{[\mathrm{Zn{-}Br}(i)]_{\max} - [\mathrm{Zn{-}Br}(i)]_{\min}\}. \tag{3}$$

Table 6. *Atomic fractional coordinates of the basic structure* ($\times 10^4$) *and the Fourier coefficients of the modulation functions* ($\times 10^4$)

		293 K			140 K			95 K		
	i	x_{0i}	d_{ic}	d_{is}	x_{0i}	d_{ic}	d_{is}	x_{0i}	d_{ic}	d_{is}
Rb(1)	1	3234 (1)	0	0	3229 (1)	23 (3)	−24 (3)	3223 (1)	3 (5)	−15 (4)
	2	2500	−11 (5)	−147 (4)	2476 (8)	149 (3)	167 (3)	2489 (10)	174 (4)	204 (4)
	3	5153 (1)	0	0	5127 (1)	0 (4)	−14 (5)	5120 (2)	23 (6)	−3 (6)
Rb(2)	1	5968 (1)	0	0	5970 (2)	20 (5)	53 (4)	5970 (2)	27 (6)	50 (6)
	2	2500	110 (5)	91 (5)	2530 (9)	−195 (4)	−34 (4)	2519 (12)	−223 (5)	−28 (5)
	3	8730 (1)	0	0	8759 (2)	16 (5)	−28 (5)	8765 (2)	6 (7)	−25 (6)
Zn	1	5777 (1)	0	0	5785 (1)	−6 (3)	10 (4)	5789 (1)	−7 (6)	−8 (6)
	2	2500	−30 (4)	93 (4)	2491	−17 (3)	−137 (3)	2497	−16 (4)	−132 (4)
	3	2746 (1)	0	0	2766 (1)	1 (5)	−11 (5)	2772 (2)	37 (7)	−18 (6)
Br(1)	1	5831 (1)	0	0	5803 (1)	−27 (3)	−46 (3)	5792 (1)	−27 (5)	−52 (5)
	2	2500	−60 (6)	349 (5)	2479 (8)	−169 (5)	−508 (4)	2497 (10)	−172 (6)	−560 (5)
	3	5184 (1)	0	0	5224 (1)	40 (4)	7 (4)	5234 (2)	20 (5)	−16 (6)
Br(2)	1	4126 (1)	0	0	4146 (1)	−1 (3)	13 (3)	4157 (1)	−3 (5)	6 (4)
	2	2500	−516 (5)	59 (7)	2603 (8)	545 (5)	−438 (5)	2619 (9)	593 (6)	−490 (7)
	3	1802 (1)	0	0	1756 (2)	4 (5)	−23 (4)	1740 (2)	−2 (6)	−33 (6)
Br(3)	1	6593 (1)	−252 (2)	1 (3)	6687 (2)	291 (3)	−178 (3)	6704 (3)	316 (4)	−218 (4)
	2	5012 (1)	183 (3)	62 (4)	4966 (6)	−243 (5)	62 (4)	4941 (8)	−243 (7)	107 (6)
	3	1839 (1)	−118 (3)	−92 (3)	1910 (3)	240 (4)	58 (4)	1922 (3)	283 (4)	46 (4)
Br(4)	1				6569 (2)	−297 (3)	182 (3)	6580 (3)	−315 (4)	200 (4)
	2				−47 (6)	−278 (5)	85 (5)	−64 (8)	−276 (6)	105 (6)
	3				1858 (3)	−184 (4)	−9 (3)	1888 (3)	−203 (4)	−46 (4)

The structures at 293 and 95 K do indeed have quite small values of D: 0·037 and 0·025 Å respectively. However, the resulting structure at 140 K [using the weighting scheme $w_r = 1/\sigma^2(F_o)$] has a quite large value: $D = 0{\cdot}056$ Å. Assuming that the absorption correction at this temperature is slightly unsatisfactory, a weighting scheme $w_r = 1/[\sigma^2(F_o) + (0{\cdot}05F_o)^2]$ was used. This weighting scheme gives a lower weight to stronger reflections. If something is wrong with the absorption correction, then those reflections will be more affected than weaker ones. The result is shown in Table 5: the value of D is smaller for the new weighting scheme. Therefore, the structure produced by this refinement is considered to be a better approximation to the real crystal structure of Rb_2ZnBr_4 at 140 K.

Many attempts were made to refine the room-temperature structure with space group $Pc2_1n(00\gamma)(s\bar{1}\bar{1})$, using 1678 reflections ($h^2 + k^2 + l^2 < 100$) or 1359 reflections (the 557 main reflections with $h^2 + k^2 + l^2 < 100$ and 802 satellites with $h^2 + k^2 + l^2 < 80$). These refinements did not include more reflections as that would not have changed the results significantly (compare D of refinements 2 and 3 in Table 5), and it would have required much more computation time. The number of parameters in these refinements was 100: 20 position parameters, 42 modulation parameters, 37 temperature parameters (isotropic temperature factor for Zn) and one scale factor. Several sets of starting parameters were tried, and several refinement strategies were used. Soft constraints on the Zn—Br distances [imposed by a penalty function (Yamamoto, 1983)] in the first stage of refinements were also used. The residuals resulting from these refinements were all about 0·063. According to Hamilton (1965) these values are significantly lower than the value of 0·0771 for space group $Pcmn(00\gamma)(ss\bar{1})$, but the corresponding structures have values of D above 0·09 Å (mostly about 0·12 Å). Moreover, parameters which are restrained because of symmetry in space group $Pcmn(00\gamma)(ss\bar{1})$ but unrestrained in $Pc2_1n(00\gamma)(s\bar{1}\bar{1})$, converge to strongly varying values in the different refinement trials: the x_{o2} parameters of the atoms on the pseudo-$m(s)$ plane vary more than 0·01 and the modulation parameters more than 0·005. If the structure really had space group $Pc2_1n(00\gamma)(s\bar{1}\bar{1})$, with such values for those parameters, it could be expected that most of the refinement trials would converge to those values. The variations could be caused by systematic errors in the observed structure factors remaining after absorption correction. The refined parameters will adapt to these errors, thus lowering wR and giving values deviating strongly from $Pcmn(00\gamma)(ss\bar{1})$ symmetry, because of the very strong correlations between these parameters in the least-squares procedure. This is also observed during refinements in space group $P2_12_12_1(00\gamma)(\bar{1}\bar{1}1)$. Because the initial stages of the refinements in this space group resulted in a much smaller reduction of wR than in space group $Pc2_1n(00\gamma)(s\bar{1}\bar{1})$, this space group was not investigated further.

Therefore, the room temperature structure of Rb_2ZnBr_4 is believed to be approximated best by the structure resulting from the refinement in space group $Pcmn(00\gamma)(ss\bar{1})$.

5. Results

The fractional coordinates of the basic structure and the Fourier coefficients of the modulation functions are given in Table 6 for the three structures. The actual position $\mathbf{x}$ of an atom in a given subcell of the modulated structure (incommensurate or commensurate) can be represented by

$$\mathbf{x} = \mathbf{n} + \mathbf{x}_0 + \mathbf{d}[(\mathbf{n} + \mathbf{x}_0).\mathbf{q}], \qquad (4)$$

in which $\mathbf{n}$ is the position of the subcell, $\mathbf{x}_0$ is the basic structure position of the atom, $\mathbf{q}$ is the modulation

Table 7. *Anisotropic temperature parameters* ($Å^2 \times 10^4$)

The parameters correspond to temperature factor $\exp(-2\pi^2\sum_{ik}U_{ik}h_ih_ka_i^*a_k^*)$.

	293 K			140 K			95 K		
	U_{11} U_{23}	U_{22} U_{13}	U_{33} U_{12}	U_{11} U_{23}	U_{22} U_{13}	U_{33} U_{12}	U_{11} U_{23}	U_{22} U_{13}	U_{33} U_{12}
Rb(1)	354 (6)	593 (9)	367 (6)	254 (6)	369 (8)	172 (6)	118 (9)	232 (11)	120 (9)
	0	29 (5)	0	−22 (18)	9 (5)	−1 (13)	22 (29)	2 (8)	−22 (21)
Rb(2)	1170 (14)	696 (11)	369 (8)	654 (12)	450 (11)	176 (7)	444 (13)	396 (13)	112 (10)
	0	−55 (8)	0	−8 (19)	−6 (7)	90 (21)	60 (28)	0 (9)	−8 (32)
Zn	296 (7)	279 (7)	292 (7)	217 (6)	210 (7)	140 (6)	90 (11)	104 (11)	60 (10)
	0	−4 (5)	0	4 (18)	0 (5)	−2 (16)	23 (27)	1 (9)	−27 (33)
Br(1)	602 (9)	1152 (18)	240 (6)	376 (8)	540 (13)	119 (6)	178 (12)	345 (17)	65 (9)
	0	−74 (6)	0	−23 (15)	−36 (6)	−81 (16)	0 (24)	−23 (9)	−79 (25)
Br(2)	338 (7)	1165 (22)	414 (8)	258 (7)	581 (12)	200 (7)	137 (10)	441 (17)	126 (11)
	0	−121 (6)	0	−10 (17)	−54 (6)	53 (15)	30 (23)	−60 (9)	69 (24)
Br(3)	982 (11)	378 (7)	631 (8)	604 (16)	237 (13)	291 (13)	340 (18)	146 (21)	164 (17)
	−46 (6)	250 (9)	−316 (8)	−25 (12)	133 (13)	−165 (12)	−37 (17)	78 (17)	−126 (18)
Br(4)				549 (15)	266 (14)	306 (14)	382 (19)	73 (20)	195 (19)
				10 (12)	71 (13)	90 (12)	−8 (19)	118 (17)	54 (17)

wavevector and $\mathbf{d(t)}$ is the displacement vector function, defined by its components $d_i(t)$, which are the modulation functions.

For the three structures described in this paper, the modulation functions are given by

$$d_i(t) = \mathrm{d}_{ic}\cos 2\pi t + d_{is}\sin 2\pi t. \quad (5)$$

In Table 7 the anisotropic temperature parameters are given for the three structures. The parameters in Tables 6 and 7 are the direct results of the refinements.

The modulation functions can also be written as

$$d_i(t) = A_i\cos 2\pi(t - \varphi_i), \quad (6)$$

with A_i and φ_i being respectively their amplitude and phase. The values of A_i and φ_i of the three structures are given in Table 8. To the phases at room temperature we added 5/12 in order to make them comparable with the phases of the other structures.

Table 9 lists the equivalent isotropic temperature parameters, and Table 10 gives the distances in the $ZnBr_4$ tetrahedra. These distances are not corrected for thermal motion.

The residuals for the three structures are listed in Table 1. The residuals for the main reflections alone and the satellites alone are also given. The residuals for the satellites are larger than those for the main reflections because the satellites are much weaker, on average, than the main reflections. This results in a smaller denominator in equation (2), and hence a larger *wR*.

Table 8. *Amplitudes* (A_i, $\times 10^4$) *and phases* (φ_i) *of the modulation functions*

$\frac{5}{12}$ has been added to the phases of the modulation functions in the room-temperature structure to make them comparable to the phases of the two other structures.

		293 K		140 K		95 K	
	i	A_i	φ_i	A_i	φ_i	A_i	φ_i
Rb(1)	1	0		33 (3)	0·87 (1)	15 (4)	0·78 (5)
	2	147 (4)	0·155 (4)	223 (3)	0·134 (2)	268 (4)	0·138 (3)
	3	0		14 (5)	0·75 (5)	23 (6)	0·98 (4)
Rb(2)	1	0		56 (4)	0·19 (1)	57 (6)	0·17 (2)
	2	143 (5)	0·527 (5)	198 (4)	0·527 (3)	225 (5)	0·520 (3)
	3	0		32 (5)	0·84 (2)	26 (6)	0·79 (4)
Zn	1	0		12 (4)	0·33 (5)	11 (6)	0·63 (9)
	2	98 (4)	0·716 (6)	138 (3)	0·730 (4)	133 (4)	0·731 (5)
	3	0		11 (5)	0·76 (7)	41 (7)	0·93 (3)
Br(1)	1	0		53 (3)	0·67 (1)	59 (5)	0·67 (1)
	2	354 (5)	0·694 (2)	535 (4)	0·699 (1)	585 (5)	0·702 (1)
	3	0		41 (4)	0·03 (1)	26 (5)	0·89 (3)
Br(2)	1	0		13 (3)	0·27 (4)	7 (4)	0·3 (1)
	2	520 (5)	0·899 (2)	699 (5)	0·892 (1)	769 (7)	0·890 (1)
	3	0		23 (4)	0·77 (3)	33 (6)	0·74 (3)
Br(3)	1	252 (2)	0·916 (1)	341 (3)	0·913 (1)	383 (4)	0·904 (2)
	2	193 (3)	0·468 (2)	251 (5)	0·460 (3)	265 (7)	0·434 (4)
	3	150 (3)	0·022 (3)	247 (4)	0·038 (2)	286 (4)	0·026 (2)
Br(4)	1			348 (3)	0·413 (1)	373 (4)	0·410 (2)
	2			291 (5)	0·453 (3)	295 (6)	0·442 (3)
	3			184 (4)	0·508 (3)	208 (4)	0·535 (3)

6. Discussion

By comparing the three structures in Table 8, one can see that the modulation in these structures is very similar. The modulation amplitudes are larger at lower temperatures, but the same patterns of large and small amplitudes exist in all structures, and the phases are equal to a very good approximation. This is the case despite the fact that the structure at 293 K is incommensurate (or a seventeenfold superstructure) and both others are threefold superstructures. In all three structures the largest amplitudes are A_2 of Br(1) and Br(2).

In the room-temperature structure Br(4) is exactly the *m*(*s*) image of Br(3). In both other structures, this symmetry operation does not exist. However, in the 140 and 95 K structures, Br(4) is in good approximation the *m*(*s*) image of Br(3), as can be seen from the modulation amplitudes and phases in Table 8: $d_1(t)$ and $d_3(t)$ of Br(4) are in antiphase with those of Br(3), and $d_2(t)$ is in phase with $d_2(t)$ of Br(3).

Table 10 shows that the $ZnBr_4$ tetrahedra are rather rigid, with all Zn—Br distances about equal. Also, all Br(*i*)—Br(*k*) distances are about equal for each set of *i*, *k*. But the Br(1)—Br(2) distances are systematically larger than the other ones, and the Br(1)—Br(3) and Br(1)—Br(4) distances are systematically larger than Br(2)—Br(3), Br(2)—Br(4) and Br(3)—Br(4). These systematic differences also exist in the normal phase (de

Table 9. *Equivalent isotropic temperature parameters* ($Å^2 \times 10^4$)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	293 K	140 K	95 K
Rb(1)	438 (4)	265 (4)	157 (6)
Rb(2)	745 (6)	427 (6)	317 (7)
Zn	289 (4)	189 (4)	85 (6)
Br(1)	665 (7)	345 (6)	196 (7)
Br(2)	639 (8)	346 (5)	235 (8)
Br(3)	664 (5)	377 (8)	217 (11)
Br(4)		374 (8)	217 (11)

Table 10. *Interatomic distances in the* $ZnBr_4$ *tetrahedra* ($Å \times 10^3$)

The estimated standard deviations are 0·004, 0·008 and 0·01 Å for the distances at 293, 140 and 95 K respectively.

	293 K	140 K			95 K		
Zn–Br(1)	2360 — 2370	2417	2337	2373	2374	2397	2380
Zn–Br(2)	2378 — 2409	2404	2411	2381	2414	2402	2398
Zn–Br(3)	2361 — 2414	2382	2416	2418	2394	2405	2402
Zn–Br(4)	2361 — 2414	2403	2360	2396	2433	2383	2393
Br(1)–Br(2)	3982 — 4019	4043	4026	4010	4043	4062	4013
Br(1)–Br(3)	3876 — 3937	3959	3876	3889	3944	3916	3880
Br(1)–Br(4)	3876 — 3937	3904	3858	3984	3890	3900	3991
Br(2)–Br(3)	3795 — 3874	3885	3824	3862	3895	3818	3867
Br(2)–Br(4)	3795 — 3874	3814	3868	3812	3833	3890	3833
Br(3)–Br(4)	3838 — 3900	3914	3857	3855	3926	3885	3847

Pater, 1979), and in Rb_2ZnCl_4 (Quilichini & Pannetier, 1983), K_2ZnCl_4 (Mikhail & Peters, 1979), K_2CoCl_4 (Vermin *et al.*, 1976), $(NH_4)_2ZnCl_4$ (Matsunaga, 1982), Cs_2CdBr_4 and Cs_2HgBr_4 (Altermatt, Arend, Gramlich, Niggli & Petter, 1984).

Apart from these systematic differences, the variations in the distances in $ZnBr_4$ tetrahedra are much smaller than the modulation amplitudes of the Br atoms and the Zn atoms have small modulation amplitudes. It can therefore be concluded that the modulation consists mainly of rotations of the tetrahedra.

As is discussed by Hogervorst (1986), the modulations of the three structures of Rb_2ZnBr_4 discussed here are very similar to modulated structures in other A_2BX_4 compounds.

For each structure the equivalent isotropic thermal parameters (Table 9) of the Br atoms are about equal. The thermal motion of these atoms (Table 7) is strongly anisotropic, with the larger axes in directions normal to the Zn–Br bonds, while the thermal motion of Zn is much smaller than that of the Br atoms. From this it can be concluded that the thermal motion, too, mainly involves rotation of the tetrahedra. In each of the three Rb_2ZnBr_4 structures the thermal motion of Rb(2) is much larger than that of Rb(1). This corresponds to the fact that the cage of Br atoms around Rb(2) is considerably larger than the one around Rb(1), *i.e.* Rb(2) has more space to move in.

A few questions remain: what is the actual space group of the room-temperature phase of Rb_2ZnBr_4; and what is the essential difference between phase *F* and phase IV? The results of these three structure determinations do not give a clear answer to these problems.

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The Structure and Si,Al Distribution of the Ultramarines

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Abstract

The structure and Si,Al distributions of various ultramarine pigments have been investigated using X-ray and neutron powder diffraction with Rietveld refinement, and magic-angle-spinning NMR (MAS NMR). The basic structures of the ultramarines studied are found to be very similar: refinement proceeds far better in space group $I\bar{4}3m$ than in $P\bar{4}3n$ which indicates that Si and Al in the framework of ultramarines are disordered. This conclusion is supported by ^{29}Si MAS NMR spectra which contain five signals, rather than a single signal which would be present if Al—O—Al linkages were forbidden. The intensities of the five peaks are consistent with the presence of Si—O—Si, Si—O—Al *and* Al—O—Al linkages in the structure. Such disordered Si,Al distributions in pyrolytically formed ultramarines are in striking contrast to the ordered distributions found in both the naturally formed counterpart lazurite and in hydrothermally synthesized zeolites.

Introduction

The ultramarines are a family of closely related pigments, the best example of which is Reckitt's blue with the ideal formula

$$Na_{7\cdot5}Al_6Si_6O_{24}S_{4\cdot5}.$$

The framework structure is that of sodalite, and the pigments may be obtained synthetically by furnacing a mixture of the appropriate amounts of kaolin, sulfur, sodium carbonate and minor ingredients (Beardsley & Whiting, 1948; Prener & Ward, 1950; van Order & Hill, 1950).

Historical records trace the knowledge of ultramarines to ancient times when natives of the Badaskan district of Afghanistan used pieces of an intensely blue rock as an ornament for making crude pigment. The rock formed in a calcite and dolomite matrix with small flakes of iron pyrites and became known as lapis lazuli or lazurite. Ancient legend believed it to be pieces of the night sky fallen to earth. By the Middle Ages, the material had assumed considerable importance as an expensive blue pigment.

The high cost of extracting and shipping lapis lazuli from Afghanistan led in the 1800's to chemical analyses (Desormes & Clement, 1806) and various attempts (Guimet, 1828; Gmelin, 1828) to make the pigment synthetically culminating with commercial production (in the UK by James Reckitt and Sons during the mid-1880's). From that time the rare natural pigment has been referred to as lazurite while the synthetic counterparts have adopted the name ultramarine.

The basic structure of the ultramarines was first studied by Jaeger (1929), and later by Leschewski (1935), who concluded that it is based on sodalite (Pauling, 1930; Barth, 1932). However, until the mid-1980's, there had been no substantial crystallographic analyses of this structure and no successful dynamic study of the intermediates formed during the production of ultramarines (Tarling, Barnes & Mackay, 1984) though a number of spectroscopic techniques (see below) had been brought to bear on the problem of identifying the colour groups in the various ultramarine products.

We have refined the structure of ultramarine using X-ray and neutron diffraction methods, and have probed the Si,Al distribution using magic-angle-spinning nuclear magnetic resonance. These analyses are also supported by the current literature results from other spectroscopic techniques.

Previous studies on the structure of ultramarines

Jaeger (1929) identified the three main structural components of ultramarine: the aluminosilicate cage;

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