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## Phase Transitions in RbLiSO<sub>4</sub>

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### Abstract

The structure of the commensurate modulated phase (IV) of RbLiSO<sub>4</sub> (RLS) was determined by single-crystal X-ray diffractometry at 446 K.  $M_r = 188.5$ , monoclinic,  $P11n$ ,  $a = 9.157$  (1),  $b = 5.316$  (1),  $c = 43.654$  (3) Å,  $\gamma = 89.97$  (1)°,  $U = 2125$  Å<sup>3</sup>,  $Z = 20$ ,  $D_x = 2.95$  Mg m<sup>-3</sup>,  $\text{Cu } K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 19.94$  mm<sup>-1</sup>,  $F(000) = 1760$ ,  $R = 0.091$ ,  $wR = 0.045$  for 2191 independent reflexions (including 329 unobserved reflexions). The fivefold superstructure in the  $c$  direction is mainly caused by a rotation of the sulfate tetrahedra around  $c$ . In order to show the structural changes connected with the phase transitions difference Fourier maps and probability density functions (p.d.f.'s) of phases (I) (485 K, re-refined with anharmonic temperature factors), (III) (465 K) and (IV) were calculated and all existing orientation states of the SO<sub>4</sub> groups obtained. Models of the phase transitions are discussed from a structural point of view.

### Introduction

In recent years the compounds  $MLiSO_4$  ( $M = \text{NH}_4, \text{Rb}, \text{Cs}$ ) have been the subject of many studies. Similar to such other  $A_2BX_4$ -type crystals as K<sub>2</sub>SeO<sub>4</sub> (Iizumi, Axe, Shirane & Shimaoka, 1977) or Rb<sub>2</sub>ZnBr<sub>4</sub> (Gesli & Iizumi, 1978), these substances undergo incommensurate-commensurate phase transitions and have ferroelectric and ferroelastic phases, respectively. Hahn, Lohre & Chung (1969) showed that these pseudohexagonal structures can be derived from a new type of tetrahedral framework with symmetry  $Icmm$ . Investigations on the system NH<sub>4</sub>LiSO<sub>4</sub> (ALS) by Dollase (1969), Hildmann (1980) and Itoh, Ishikura & Nakamura (1981) exhibited the transitions:

phase (I) ( $Pcmn$ )

$\xrightarrow{460 \text{ K}}$  phase (II) (ferroelectric,  $Pc2_1n$ )

$\xrightarrow{283 \text{ K}}$  phase (III) (ferroelastic,  $P12_1/c1$ ).

Kruglik, Simonov, Zhelezin & Belov (1979), Tomaszewski, Pietraszko & Lukaszewicz (1981) and Hildmann, Hahn, Heger & Guth (1983) found the transitions:

phase (I) (*Pcmn*)

$\xrightarrow{219\text{ K}}$  phase (II) (?)

$\xrightarrow{196\text{ K}}$  phase (III) (ferroelastic, *P112<sub>1</sub>/n*)

for CsLiSO<sub>4</sub> (CLS). X-ray studies on the phase transitions in RLS were performed by Mashiyama, Hasebe, Tanisaki, Shiroishi & Sawada (1979). The structure of the room-temperature phase (V) was determined by Kruglik, Misyl & Simonov (1979) and by Tanisaki, Mashiyama, Hasebe, Shiroishi & Sawada (1980). Frey, Jagodzinski, Pietraszko & Zeyen (1983) investigated the diffuse scattering and the transitions in the region of phase (I) to (III) by neutron scattering. The structures of phases (I) and (III) were solved by Pietraszko & Jagodzinski (1984). The results of these works are shown in Table 1.

The aim of the present work was to determine the unknown structure of phase (IV) and to discuss the structural changes on going from phase (I) to phase (V), in order to obtain a better insight into the mechanism of the phase transitions.

### Experimental and structure refinements

#### Phase (IV)

The preparation of the spherical crystal (diameter 0.24 mm) was as described by Pietraszko & Jagodzinski (1984). Data collection: Enraf-Nonius CAD-4 four-circle diffractometer, graphite-monochromated Cu  $K\alpha$  radiation; lattice parameters from least-squares refinement of 25 high-angle reflexions;  $\omega/2\theta$  scans. A hot-air heating device was used; the absolute temperature was calibrated on the phase transition at 439 K; the relative temperature deviations at the site of the crystal were  $< \pm 1$  K. A spherical-absorption correction ( $\mu R = 2.25$ ), and Lorentz and polarization corrections were applied in the usual way. The two data sets measured (*A*: 980 fundamental reflexions,  $-10 \leq h \leq 10$ ,  $0 \leq k \leq 6$ ,  $0 \leq l \leq 50$ ; *B*: 1691 fundamental and satellite reflexions  $-6 \leq h \leq 6$ ,  $0 \leq k \leq 4$ ,  $0 \leq l \leq 35$ ) ( $2\theta_{\max} = 70^\circ$ ) were merged using common reflexions and the linear least-squares method for deriving batch scale factors. Three orientation-control reflexions were measured every 30 collected intensities. One intensity-control reflexion was measured every 60 min, maximum deviation  $\pm 0.8\%$ . After averaging, 2195 [including 329 unobserved ( $I_{\text{obs}} \leq 0$ )] independent reflexions remained ( $R_{\text{int}} = 0.017$ ). The systematic absences  $hk0$ :  $h + k = 2n + 1$  suggest space group *P11n* (Mashiyama *et al.*, 1979). The occurrence of relatively strong satel-

Table 1. *Regions of existence, space groups and multiples of the subcell for the modulated structures of RLS (Mashiyama *et al.*, 1979)*

Phase (I)	477 < <i>T</i> K	<i>Pcmn</i>	<i>c</i> <sub>0</sub>	Disordered
Phase (II)	475 < <i>T</i> < 477 K	?	$\approx 5c_0$	Incommensurate
Phase (III)	458 < <i>T</i> < 475 K	<i>P12<sub>1</sub>/c1</i>	2 <i>c</i> <sub>0</sub>	Antiferroelectric
Phase (IV)	439 < <i>T</i> < 458 K	<i>P11n</i>	5 <i>c</i> <sub>0</sub>	Ferroelectric
Phase (V)	<i>T</i> < 439 K	<i>P112<sub>1</sub>/n</i>	<i>c</i> <sub>0</sub>	

lites of uneven order is an indication for a rectangular modulation wave. The refinements of the average structure were carried out in space group *P112<sub>1</sub>/n* because high correlations were observed between parameters connected by the pseudosymmetry element 2<sub>1</sub> (the reflexions with  $00l$ :  $l = 2n + 1$  are absent or very weak) when refining in space group *P11n*. The *R* factors did not differ significantly.

The positional parameters obtained by Pietraszko & Jagodzinski (1984) for phase (V) at 422 K were used as starting values ( $R = 0.068$ ,  $wR = 0.070$ ). Strikingly high temperature factors were calculated for the O atoms [O(1):  $U_{11} = 0.132$  (9); O(2):  $U_{11} = 0.24$  (2); O(3):  $U_{11} = 0.21$  (1); O(4):  $U_{22} = 0.37$  (3)  $\text{\AA}^2$ ] and the difference Fourier maps showed double-peaked contours. Refinements with split O atoms yielded  $R = 0.049$ ,  $wR = 0.051$  and after omission of the reflexions 020, 330,  $\bar{3}30$  and 040, presumably strongly affected by extinction, the final  $R = 0.046$ ,  $wR = 0.044$  (96 parameters, 799 observed reflexions).

The refinements of the superstructure started with the average parameters. In order to bring the number of variables to a reasonable relation to the number of observations (70 independent atoms with 630 atomic parameters) and to avoid strong correlations between the equivalent atoms of different subcells, some parameters had to be constrained or fixed. The *x*, *y*, *z* coordinates of Li, the *x* and *z* of Rb and the *z* of the S and O(1) were fixed to average values because the  $U_{ij}$  values of these atoms behaved quite normally in the average structure. In addition, O(*i*)–O(*j*) bond-length constraints were applied. The O tetrahedra of all subcells were forced to adopt the same size with an error of 0.01  $\text{\AA}$  in the refinements. This increases the number of variables (one for each edge of the tetrahedron) by 6. The anisotropic temperature factors of the atoms in the subcells with an equivalent orientation of the SO<sub>4</sub> group were set to the same value in the refinements.

The final  $R = 0.069$ ,  $wR = 0.045$  (overall, 208 variables, 1862 observed reflexions),  $R = 0.091$  (including unobserved reflexions), and  $R = 0.25$ ,  $wR = 0.082$  (973 satellite reflexions only) were obtained.  $(\Delta/\sigma)_{\max} = 0.61$ . A refinement using the superstructure reflexions only yielded  $R = 0.21$ ,  $wR = 0.056$  with no principal changes of the atomic parameters. The rather high unweighted satellite *R* factor may be due to the temperature instability during the data collection and not well separated diffuse scattering. These

factors influence the large number of weak reflexions most. All calculations had to be performed with a damping factor to prevent oscillation around the  $R$ -factor minimum.

### Phase (I)

The data set collected by Pietraszko & Jagodzinski (1984) was used for the calculations. The refinements were performed on an ordered model with harmonic ( $R = 0.046$ ,  $wR = 0.049$ , 41 variables, 453 reflexions) and anharmonic temperature factors ( $R = 0.024$ ,  $wR = 0.026$ , 77 variables, up to fourth-rank tensors used). The disordered model, with split O atoms, gave  $R = 0.030$ ,  $wR = 0.031$  for 56 variables. In order to reduce the number of variables for the refinements with anharmonic temperature factors all temperature coefficients with values smaller than their e.s.d.'s were set to zero and fixed (77 instead of 108 variables). A refinement with all possible variables yielded the same  $R$  factors. Difference Fourier and p.d.f. maps were calculated.

The data reduction was performed with the *Structure Determination Package* of Enraf-Nonius (Frenz, 1978), and merging and averaging and the structure refinements (on  $F$ ) with the program *SHELX76* (Sheldrick, 1976) on a Cyber 175 computer. The refinements of anharmonic temperature factors and the calculation of the p.d.f. maps were carried out with the program *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983). Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Weights assigned to the reflexions:  $w = 1/\sigma^2(F_o)$ .

## Results

### Phase (IV)

The final atomic parameters are listed in Table 2.\* The ordering of the  $SO_4$  groups is displayed in Fig. 1. The modulation can be described schematically by a rectangular wave (see Fig. 2). If a right(left)-hand rotation of the tetrahedra around  $c$  is denoted by  $+(-)$  then the ordering in the  $O(i)$  layers succeeding one another can be described by  $+-+-+---+---$  [phase (I):  $\pm\pm$ ; phase (III):  $+-+-$ ; phase (V):  $+-$  (Pietraszko & Jagodzinski, 1984)]. This sequence (or the alternative one  $--+---+---++$ ) can also be derived by theoretical considerations: the three tetrahedra of one  $O(i)$  layer around one Rb atom

\* Lists of structure factors, anisotropic thermal parameters and results of thermal-motion analyses have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42458 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates and temperature factors ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses for the superstructure and the average structure (labelled 'ave') of phase (IV) of RLS

	x	y	z	$U_{eq}/U_{iso}^*$
Rb(1)	0.2833	0.2488	0.0005	0.0382
Rb(2)		0.229 (2)	0.2005	
Rb(3)		0.250 (2)	0.4005	
Rb(4)		0.236 (2)	0.6005	
Rb(5)		0.232 (2)	0.8005	
Rb(1A)	0.7167	0.732 (2)	0.9995	
Rb(2A)		0.749 (2)	0.7995	
Rb(3A)		0.742 (2)	0.5995	
Rb(4A)		0.736 (2)	0.3995	
Rb(5A)		0.748 (2)	0.1995	
Rb <sub>ave</sub>	0.2833 (1)	0.2488 (1)	0.0025 (1)	0.0392
Li(1)	0.416	0.748	0.066	0.036 (2)
Li(2)			0.266	
Li(3)			0.466	
Li(4)			0.666	
Li(5)			0.866	
Li(1A)	0.584	0.252	0.934	
Li(2A)			0.734	
Li(3A)			0.534	
Li(4A)			0.334	
Li(5A)			0.134	
Li <sub>ave</sub>	0.416 (2)	0.748 (4)	0.328 (2)	0.043
S(1)	0.084 (2)	0.735 (3)	0.0412	0.0212
S(2)	0.077 (2)	0.734 (2)	0.2412	
S(3)	0.077 (2)	0.733 (3)	0.4412	
S(4)	0.077 (2)	0.756 (3)	0.6412	
S(5)	0.080 (2)	0.750 (3)	0.8412	
S(1A)	0.918 (2)	0.246 (3)	0.9588	
S(2A)	0.914 (2)	0.233 (3)	0.7588	
S(3A)	0.914 (2)	0.243 (3)	0.5588	
S(4A)	0.910 (2)	0.240 (3)	0.3588	
S(5A)	0.913 (2)	0.243 (3)	0.1588	
S <sub>ave</sub>	0.0825 (2)	0.7503 (5)	0.2059 (3)	0.0220
O(11)	0.109 (3)	0.750 (4)	0.0082	0.050
O(12)	0.094 (3)	0.750 (4)	0.2082	0.063
O(13)	0.107 (3)	0.753 (4)	0.4082	0.050
O(14)	0.092 (3)	0.741 (4)	0.6082	0.063
O(15)	0.100 (3)	0.741 (4)	0.8082	0.063
O(11A)	0.927 (3)	0.232 (4)	0.9918	0.050
O(12A)	0.913 (3)	0.249 (4)	0.7918	0.063
O(13A)	0.935 (3)	0.262 (4)	0.5918	0.050
O(14A)	0.907 (3)	0.241 (4)	0.3918	0.063
O(15A)	0.913 (3)	0.256 (4)	0.1918	0.063
O(1) <sub>ave</sub>	0.091 (1)	0.750 (2)	0.0409 (9)	0.070
O(21)	0.048 (2)	0.996 (2)	0.0515 (4)	0.037
O(22)	0.951 (2)	0.911 (3)	0.2489 (6)	0.049
O(23)	0.050 (2)	0.999 (2)	0.4518 (6)	0.037
O(24)	0.949 (2)	0.925 (3)	0.6475 (6)	0.049
O(25)	0.952 (2)	0.909 (3)	0.8477 (6)	0.049
O(21A)	0.947 (2)	0.007 (2)	0.9453 (4)	0.037
O(22A)	0.023 (2)	0.071 (3)	0.7478 (5)	0.049
O(23A)	0.952 (2)	0.009 (2)	0.5474 (4)	0.037
O(24A)	0.017 (2)	0.068 (3)	0.3475 (5)	0.049
O(25A)	0.011 (2)	0.057 (3)	0.1479 (5)	0.049
O(2) <sub>ave</sub>	0.999 (2)	0.951 (2)	0.257 (1)	0.129
O(31)	0.965 (2)	0.572 (3)	0.0481 (6)	0.041
O(32)	0.043 (2)	0.492 (2)	0.2514 (5)	0.043
O(33)	0.958 (2)	0.581 (3)	0.4476 (5)	0.041
O(34)	0.032 (2)	0.501 (2)	0.6524 (4)	0.043
O(35)	0.043 (2)	0.490 (2)	0.8516 (4)	0.043
O(31A)	0.037 (2)	0.427 (3)	0.9485 (5)	0.041
O(32A)	0.945 (2)	0.499 (2)	0.7472 (4)	0.043
O(33A)	0.009 (2)	0.446 (3)	0.5446 (4)	0.041
O(34A)	0.931 (2)	0.491 (2)	0.3470 (4)	0.043
O(35A)	0.935 (2)	0.485 (2)	0.1453 (4)	0.043
O(3) <sub>ave</sub>	0.025 (2)	0.524 (2)	0.261 (1)	0.116
O(41)	0.217 (2)	0.661 (3)	0.0563 (4)	0.048
O(42)	0.205 (2)	0.843 (3)	0.2558 (5)	0.055
O(43)	0.211 (2)	0.652 (3)	0.4563 (4)	0.048
O(44)	0.201 (2)	0.843 (3)	0.6558 (5)	0.055
O(45)	0.205 (2)	0.839 (3)	0.8563 (4)	0.055
O(41A)	0.781 (2)	0.349 (3)	0.9494 (5)	0.048
O(42A)	0.770 (2)	0.167 (3)	0.7478 (5)	0.055
O(43A)	0.763 (2)	0.312 (3)	0.5519 (6)	0.048
O(44A)	0.763 (2)	0.150 (3)	0.3484 (5)	0.055
O(45A)	0.759 (2)	0.156 (3)	0.1500 (6)	0.055
O(4) <sub>ave</sub>	0.222 (1)	0.779 (4)	0.268 (1)	0.162

\*  $U_{eq} = \frac{1}{3} (U_{11} + U_{22} + U_{33})$ ;  $U_{iso}$  is the isotropic temperature factor for Li.

Table 3. Ranges and means of interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the ten independently refined  $\text{SO}_4$  and  $\text{LiO}_4$  tetrahedra

	Range	Mean
S-O(1)	1.44-1.47	1.45 (1)
S-O(2)	1.39-1.53	1.46 (5)
S-O(3)	1.39-1.53	1.47 (5)
S-O(4)	1.38-1.53	1.45 (4)
O(2)-S-O(1)	105-113	109 (3)
O(3)-S-O(1)	106-113	109 (3)
O(3)-S-O(2)	106-114	109 (2)
O(4)-S-O(1)	105-114	109 (3)
O(4)-S-O(2)	105-113	110 (3)
O(4)-S-O(3)	106-114	110 (3)
Li-O(1)	1.82-2.08	1.9 (1)
Li-O(2)	1.86-1.99	1.91 (5)
Li-O(3)	1.88-2.05	1.93 (6)
Li-O(4)	1.86-2.16	2.0 (1)
Shortest distances		
Rb-O	2.78-2.93	2.87 (5)
Constrained bond lengths		
O(1)-O(2)		2.37 (1)
O(1)-O(3)		2.38 (1)
O(1)-O(4)		2.37 (1)
O(2)-O(3)		2.38 (1)
O(2)-O(4)		2.37 (1)
O(3)-O(4)		2.38 (1)

The six edges  $\text{O}(i)\text{-O}(j)$  of the  $\text{SO}_4$  tetrahedra were constrained, i.e. all equivalent distances of the ten  $\text{SO}_4$  tetrahedra were set to the same value within an error of 0.01  $\text{\AA}$ .

have to be rotated in the same sense for steric reasons. This is true for all  $\text{O}(i)$  layers and it follows that the three tetrahedra stacks have the same modulation waves with the same phases. Because of the

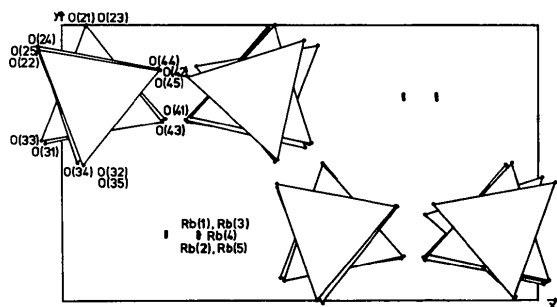


Fig. 1. Ordering of the  $\text{SO}_4$  groups in phase (IV) of RLS (viewed along  $c$ ).

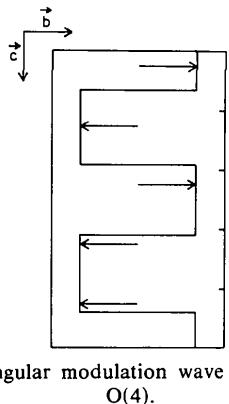


Fig. 2. The rectangular modulation wave ( $q = 0.4c^*$ ) acting on  $\text{O}(4)$ .

$n$ -glide plane (converting  $q$  to  $-q$ ) only a special value for the phase is possible (for a sine function:  $\pi/2$ ).

The Rb atoms show slight shifts parallel to  $b$  only. Table 3 gives the ranges and means of the interatomic distances. The difference Fourier synthesis exhibits maxima in the alternative orientation states of the tetrahedra (about  $0.5 e \text{\AA}^{-3}$ ). This indicates the existence of a small amount of domains with the alternative orientation of the  $\text{SO}_4$  groups and explains the unusually high anisotropic temperature-factor components of some atoms [ $\text{O}(1)$ :  $U_{11} = 0.124$  (4);  $\text{O}(4)$ :  $U_{22} = 0.073$  (3),  $U_{33} = 0.076$  (3)  $\text{\AA}^2$ ].

### Phases (I), (III) and (V)

Fig. 3 shows the difference Fourier maps for the regions around  $\text{O}(4)$  for all phases and Fig. 4 the p.d.f. maps of the O atoms of phase (I). In Table 4 (deposited) the results of a thermal-motion analysis (Schomaker & Trueblood, 1968), calculated with the program XANADU (Roberts & Sheldrick, 1976), are reported for the ordered harmonic model showing a second libration around  $b$  ( $14.2^\circ$ ) in addition to the main one around  $c$  ( $21.1^\circ$ ). The values for phase (V) at 422 K are  $10.6$  and  $6.9^\circ$ .

### Discussion of the structural relationships between the phases of RLS

The possible orientation states of the  $\text{SO}_4$  tetrahedra in the different phases of RLS can be derived by analysing the p.d.f. maps (Fig. 4) and the results of the split-atom calculations. The trajectory of an  $\text{O}(4)$  atom, changing from the + to the - position, is an ellipse as can be expected for steric reasons. The  $\text{O}(1)$  atom, performing a displacement in the  $xz$  plane at the same time, may be mainly responsible for the correlation of the rotation of the tetrahedra of neighbouring layers. The p.d.f. indicates that a high proportion of  $\text{SO}_4$  groups are in intermediate positions. Even at lower temperatures, peaks can be found in the difference Fourier maps at the alternative and intermediate orientations (Fig. 3). Of course, nothing can be said from our experiment about the dynamic or static character of these findings.

Broad maxima on the diffuse streaks parallel to  $c^*$ , precursor effects of the second-order phase transition, are observable in phase (I) at the sites of the satellite reflexions of phase (II) up to at least 510 K (Frey *et al.*, 1983). This means that small regions with the symmetry of the modulated phase (II) are coexisting with statistically distributed domains of local symmetry  $P112_1/n$  [the + and - orientation of the low-temperature phase (V) and all general intermediate positions] and  $Pcmm$  [special position with  $\text{O}(1)$  and  $\text{O}(4)$  on the reflexion plane]. Therefore the structure of phase (I) (at 485 K) will not be very different from the average structure of phase (II) and a model for

the modulated structure can be derived. The (3+1)-dimensional Bravais class (de Wolff, Janssen & Janner, 1982)  $P_{111}^{Pm\bar{m}m}(00\gamma)$  and the superspace groups  $P_{111}^{Pc\bar{m}n}(00\gamma)$  or  $P_{1s1}^{Pc\bar{m}n}(00\gamma)$  come into question. A modulation with displacements of the O(4) atoms in the reflexion plane would be consistent with the first superspace group and with shifts perpendicular to it with the second one. A rotational modulation, moving the O(4) atom on an ellipse, would be forbidden by symmetry. Owing to the maxima of the p.d.f. and the structure of the locked-in phase (III) the superspace group  $P_{1s1}^{Pc\bar{m}n}(00\gamma)$  is more probable. Consequently, the modulation should be very similar to that of phase (IV) [which has the pseudosymmetry  $P_{1s1}^{Pc\bar{m}n}(00\gamma)$ ] and the same phase relationships should hold. Then the incommensurate wave can be described by a structure of +, - microdomains with fluctuating size (see, for example, Böhm, 1983). The statistical character of the incommensurate wave will be expressed in high phase fluctuations which are not present in the commensurate case of phase (IV). Starting from a distribution like +++/---/++/

---/... with a wavelength of about  $2.5c$  a locked-in transition occurs with  $\lambda=2c$  leading to the structure of phase (III) ++/--/++/--/...

The ordered phases show two characteristic coordination polyhedra  $A$  and  $P$  for the Rb atoms. The sequence +- (or -+) forms a trigonal antiprism  $A$  and ++ (or --) a trigonal prism  $P$  as coordination polyhedron using the atoms O(2,  $i$ ), O(3,  $i$ ), O(4,  $i$ ) and O(2,  $j$ ), O(3,  $j$ ), O(4,  $j$ ) ( $i, j$  denote different layers of  $SO_4$  groups) (see Fig. 1). There are, additionally, three O(1,  $i$ ) atoms at about the same distances outside of the prisms. An ordered phase (I) would exhibit large hexagonal prisms as coordination polyhedra which could be stable for large cations only. Consequently, the tetrahedra are rotated around  $c$  to obtain a better coordination of the Rb atom. The smaller the cation the higher is the temperature at which the ordering starts. This can be seen by a comparison of the ranges of existence of the disordered phases of ALS ( $T > 460$  K), RLS ( $T > 477$  K) and CLS ( $T > 219$  K) with the size of the cations ( $r_{NH_4^+} = 1.43$ ,  $r_{Rb^+} = 1.48$ ,  $r_{Cs^+} = 1.69$  Å).

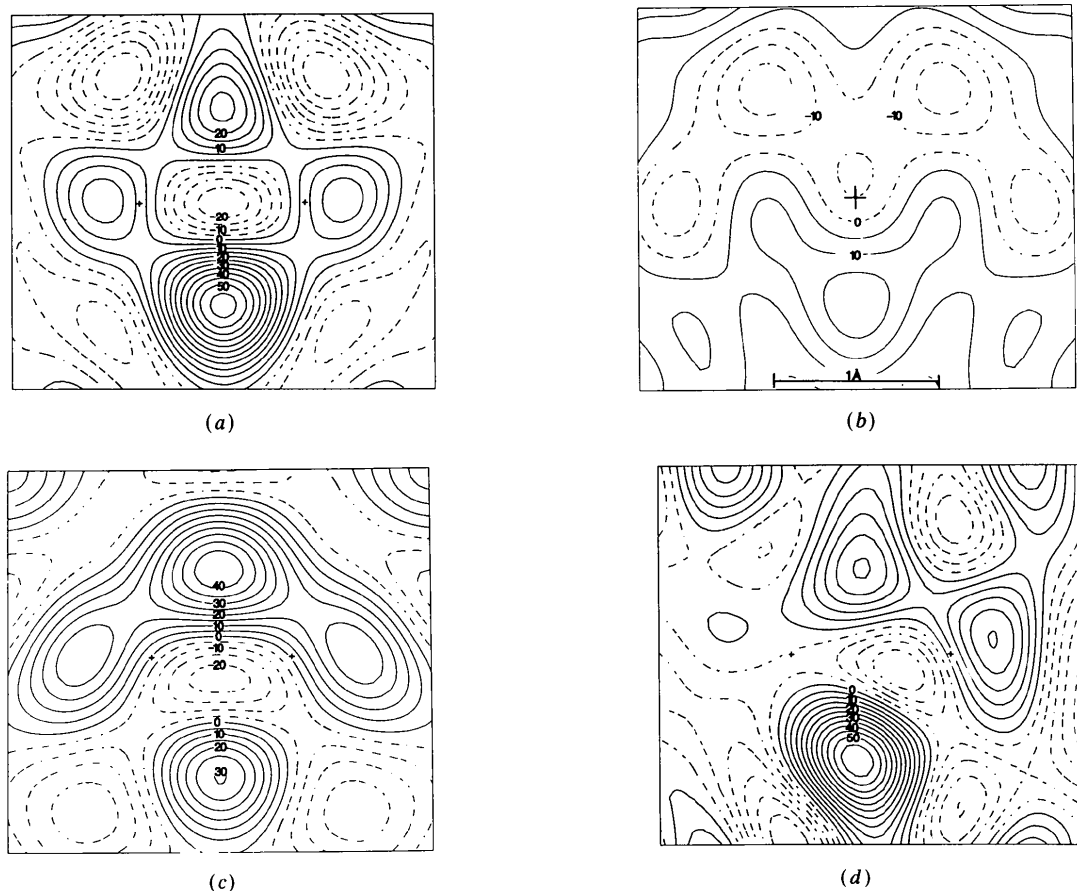
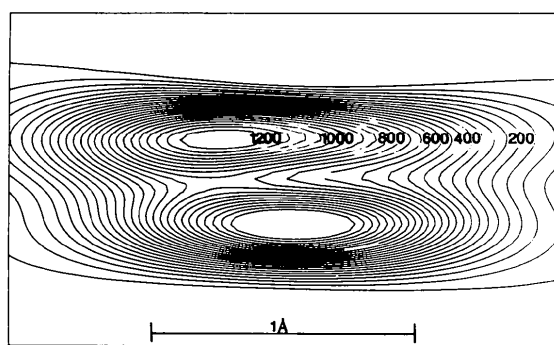
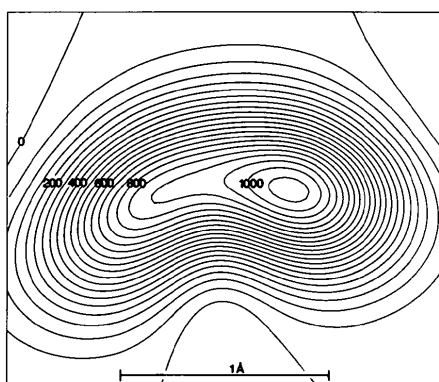


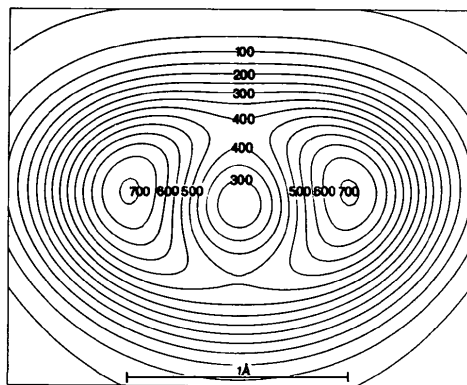
Fig. 3. Difference Fourier maps ( $\times 10^{-2} e \text{ \AA}^{-3}$ ) of (a) the two-atom split model, (b) the anharmonic model of phase (I), and the split model of the average structures of (c) phase (III) and (d) phase (IV) of RLS. The section with maximal residual density around O(4), corresponding to the plane defined by the split atoms, was chosen.



(a)



(b)



(c)

Fig. 4. P.d.f. maps ( $\text{\AA}^{-3}$ ) of the O atoms of phase (I) of RLS. (a) O(1), (b) O(2) and (c) O(4). The section with maximal density, corresponding to the planes defined by the split atoms, was chosen.

A stepwise substitution of Rb by Cs results in an increase of the stability range of the disordered phase and in a reduction of the number of possible phases (Tomaszewski *et al.*, 1981). The fraction of *A* polyhedra increases with decreasing temperature from 50% [phase (III)], over 60% [phase (IV)] to 100% [phase (V)]. These different distributions may contribute to the stabilization of the intermediate phases.

This work is a contribution to the understanding of the variety of phases of RLS by an analysis of the structural relationships between them. Many questions remain open for future work, especially the reason for the formation of the two- and fivefold superstructures and the character of the phase transitions (I)–(II)–(III).

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