

Fig. 2. A packing diagram showing the arrangement of molecules as viewed along the *a* axis.

and back donation of free-electron pairs on the O atom to an S atom polarized by its halogen substituents (Hencher & Bauer, 1973). This effect is even more pronounced in  $F_5SOSF_5$  (solid state) (Oberhammer & Seppelt, 1978), where a short S—O bridging distance [1.586 (11) Å] is compensated for by increased S—F bond lengths [1.560 (4) Å] and the large S—O—S angle of 142.5 (16)° can be attributed to both steric hindrance and a significant  $\pi$  contribution to the S—O—S bonds compared with tetrahedrally coordinated polysulfuryl halides.

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## Low-Temperature Commensurate Phase of Potassium Tetrachlorozincate, $K_2ZnCl_4$

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**Abstract.**  $K_2ZnCl_4$ ,  $M_r = 285.4$ , monoclinic,  $Cc$ ,  $a = 14.394$  (7),  $b = 24.544$  (8),  $c = 26.616$  (5) Å,  $\beta = 89.98$  (3)°,  $V = 9405.0$  (56) Å<sup>3</sup>,  $Z = 48$ ,  $D_x = 2.42$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 5.546$  mm<sup>-1</sup>,  $F(000) = 6528$ ,  $T = 140$  K, final  $R = 0.043$  for 7124 independent reflections with  $F > 5\sigma(F)$ . The structure is modified a little from the room-temperature commensurate phase of  $P2_1cn$  ( $Z = 12$ ). The  $ZnCl_4$  tetrahedra that have rather large thermal parameters at room temperature deviate especially from the  $P2_1cn$  structure by shifts along

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### References

- COSIER, J. & GLAZER, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.  
 GOULD, R. O. & TAYLOR, P. (1985). *CALC*. Program for molecular geometry calculations. Univ. of Edinburgh, Scotland.  
 GUNDERSON, G. & HEDBERG, J. (1969). *J. Chem. Phys.* **51**, 2500–2507.  
 HAYEK, E. & KOLLER, W. (1951). *Monatsh. Chem.* **82**, 942–943.  
 HENCHER, J. L. & BAUER, S. H. (1973). *Can. J. Chem.* **51**, 2047–2054.  
 MALLINSON, P. D. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.  
 MOOTZ, D. & MERSCHENZ-QUACK, A. (1988). *Acta Cryst.* **C44**, 924–925.  
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 OBERHAMMER, H. & SEPPELT, K. (1978). *Angew. Chem.* **90**, 66–67; *Angew. Chem. Int. Ed. Engl.* **17**, 69–70.  
 PAULING, L. (1952). *The Nature of the Chemical Bond*, 2nd ed. Oxford Univ. Press.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.  
 TOUŽÍN, J. & ČERNÍK, M. (1992). *Collect. Czech. Chem. Commun.* In the press.

the *a* axis and rotation about axes parallel to the *c* axis.

**Introduction.**  $K_2ZnCl_4$  is a ferroelectric compound that performs the normal-incommensurate and the incommensurate-commensurate transitions (Gesi, 1978; Gesi & Iizumi, 1979), as does  $K_2SeO_4$  (Iizumi, Axe, Shirane & Shimaoka, 1977). The crystal structures of the normal phase above 553 K and the incommensurate phase between 403 and 553 K have been analyzed by Quilichini, Bernede, Lefebvre &

Schweiss (1990). The structure of the commensurate (ferroelectric) phase at room temperature has been reported by Mikhail & Peters (1979).

In addition to the above mentioned transitions, many  $A_2BX_4$ -type crystals with  $A = K, Rb, B = Zn, Co$  and  $X = Cl, Br$  undergo further transitions at lower temperatures as summarized in the review article by Cummins (1990). In  $K_2ZnCl_4$ , the transition temperature is 145 K, below which the primitive-cell volume is doubled and the space group is considered to be a monoclinic one from NQR (Millia, Kind & Slak, 1983) and Raman scattering (Sekine, Takayama, Uchinokura & Matsuura, 1986). But, to the author's knowledge, no structure analysis has been reported.

Recently Gesi (1990) observed superlattice reflections below about 145 K by neutron scattering. He also reported that there is another incommensurate phase in a narrow temperature range between 144.5 and 148.0 K. However, a highly resolved study of X-ray scattering indicated that only diffuse scattering intensity can be observed in this temperature range (Hasebe, 1990).

In order to obtain structural information about the transition at 145 K, we have analyzed the crystal structure of the low-temperature commensurate phase of  $K_2ZnCl_4$ . In this report crystal axes are chosen so that the space group of the normal phase is  $Pm\bar{c}n$  ( $Z = 4$ ) and that of the room-temperature commensurate phase is  $P2_1cn$  ( $Z = 12$ ). Namely, the pseudo-hexagonal axis is the  $c$  axis and the polar axis is the  $a$  axis, throughout the sequence of transitions.

**Experimental.** Colorless and transparent crystals of  $K_2ZnCl_4$ , grown by slow evaporation of an aqueous solution of a stoichiometric mixture of  $KCl$  and  $ZnCl_2$  at about 310 K, were blocks with dimensions of a few mm. A spherical specimen with radius 0.245 mm was coated with epoxy-type adhesive to protect it from moisture, and was used for data collection on an automatic four-circle diffractometer (Rigaku AFC-5) with graphite-monochromated  $Mo K\alpha$  radiation. The temperature of the sample was kept at 140.0 (5) K by controlling the nitrogen gas flow. Cell dimensions were determined from 24 reflections ( $\pm 12, \pm 8, \pm 3, \pm 2, \pm 20, \pm 9$  and  $\pm 4, \pm 2, \pm 21$ ) with  $17.3 < \theta < 18.7^\circ$ . The  $\theta$ - $2\theta$  scan mode, with scan speed  $12^\circ \text{ min}^{-1}$  and scan width  $(1.2 + 0.5 \tan \theta)^\circ$ , was used to collect data over the ranges  $-10 \leq h \leq 10, 0 \leq k \leq 17, 0 \leq l \leq 19$  for  $\theta < 15^\circ$ , and  $0 \leq h \leq 20, 0 \leq k \leq 34, 0 \leq l \leq 37$  for  $15 \leq \theta < 30^\circ$ . Five standard reflections, monitored every 100 observations, showed no significant variation. 8744 reflections were measured for  $h + k = \text{even}$ . Lorentz and polarization corrections were made. Absorption correction was made by numerical integration; transmission-factor ranges from 0.156 to 0.182.

From systematic absences in all reflections, including  $h + k = \text{odd}$ , the space group was confirmed as  $C1c1, Z = 48$ , although the superlattice reflections with  $h, k = \text{odd}$  were all weak. Among strong reflections [ $F_o > 5\sigma(F_o)$ ] within the 8744 reflections for  $h + k = \text{even}$ , four did not satisfy the  $c$ -glide symmetry and were discarded as incorrect intensities affected by adjacent strong reflections. 7178 unique reflections were used for structure analysis. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). In the block-diagonal least-squares calculations,  $wR^2 = \sum w(|F_c| - |F_o|)^2 / \sum w|F_o|^2$  was minimized with unit weight. The program system *AXS89* (Mashiyama, 1991) was used and calculations were made on a personal computer.

Starting from the room-temperature structure (Mikhail & Peters, 1979), after several cycles of isotropic refinement the  $R$  value converged to 0.10. Then the random mixing of the monoclinic domains was assumed with the averaged structure factors given by  $|F_c(h, k, l)|^2 = x_{dm}|F(h, k, l)|^2 + (1 - x_{dm}) \times |F(-h, k, l)|^2$ , where  $x_{dm}$  was the volume fraction of a monoclinic domain. The  $R$  value reduced to 0.08. Finally, anisotropic thermal parameters were adopted and the calculations converged to  $R = 0.043, wR = 0.049, S = 12.3, (\Delta/\sigma)_{\text{max}} < 0.30, -1.48 < \Delta\rho < 0.82 \text{ e } \text{\AA}^{-3}$  with  $x_{dm} = 0.575$ .

**Discussion.** The final atomic parameters are listed in Table 1;\* these are very similar to those in the corresponding phase of  $K_2CoCl_4$  (Mashiyama, 1991). Two kinds of K ion which have different environments are denoted by K(1) and K(2). Although only two K ions are independent in the normal phase, 24 K ions become independent because of the cell doubling and the symmetry lowering. They are distinguished by adding letters ( $a-l$ ) to the atom number (1 and 2). The  $ZnCl_4$  tetrahedra are also labeled using letters. The structure projected along the  $a$  axis is shown in Fig. 1. The basic (the mean) structure is almost isomorphous with  $\beta$ - $K_2SO_4$  (Wyckoff, 1965). Three K(1) ions and three  $ZnCl_4$  tetrahedra construct six-membered rings, which are piled up to form pseudo-hexagonal networks as shown in Fig. 2. The other potassium ion K(2) is located at the center of the rings.

The room-temperature structure is considered to be the modulated structure of the normal phase ( $\beta$ - $K_2SO_4$ -type structure). The modulation can be characterized by translations of the constituent

\* Lists of structure factors, anisotropic thermal parameters and detailed bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55491 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic parameters and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^2$ ) with e.s.d.'s in parentheses for  $\text{K}_2\text{ZnCl}_4$  at 140 K

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	$U_{\text{eq}}$
K(1a)	0.1153†	0.0808 (2)	0.2100†	2.04 (12)
K(1b)	0.1319 (4)	0.0822 (2)	0.5431 (2)	2.38 (13)
K(1c)	0.1398 (4)	0.0778 (2)	0.8808 (2)	2.92 (16)
K(1d)	0.1594 (4)	0.4148 (2)	0.0436 (2)	2.59 (13)
K(1e)	0.1315 (4)	0.4126 (2)	0.3804 (2)	2.24 (13)
K(1f)	0.1148 (4)	0.4110 (2)	0.7111 (2)	1.82 (11)
K(1g)	0.3685 (4)	0.3319 (2)	0.2905 (2)	2.32 (13)
K(1h)	0.3959 (4)	0.3391 (2)	0.6197 (2)	2.32 (13)
K(1i)	0.4092 (4)	0.3310 (2)	0.9564 (2)	2.35 (13)
K(1j)	0.3843 (4)	0.1721 (2)	0.1206 (2)	2.26 (13)
K(1k)	0.3822 (4)	0.1604 (2)	0.4573 (2)	2.62 (14)
K(1l)	0.3556 (4)	0.1659 (2)	0.7918 (2)	1.98 (12)
K(2a)	0.1126 (3)	0.2822 (2)	0.1682 (2)	1.19 (10)
K(2b)	0.1532 (3)	0.2805 (2)	0.4983 (2)	1.34 (10)
K(2c)	0.1123 (4)	0.2812 (2)	0.8344 (2)	1.60 (11)
K(2d)	0.1505 (3)	0.2194 (2)	0.0002 (2)	1.32 (11)
K(2e)	0.1113 (3)	0.2188 (2)	0.3304 (2)	1.43 (11)
K(2f)	0.1284 (4)	0.2166 (2)	0.6650 (2)	1.77 (12)
K(2g)	0.4071 (3)	0.0288 (2)	0.0018 (2)	1.24 (10)
K(2h)	0.3738 (3)	0.0347 (2)	0.3334 (2)	1.51 (11)
K(2i)	0.3678 (3)	0.0305 (2)	0.6677 (2)	1.38 (11)
K(2j)	0.3607 (3)	0.4685 (2)	0.1697 (2)	1.17 (10)
K(2k)	0.3992 (3)	0.4678 (2)	0.5001 (2)	1.09 (10)
K(2l)	0.3701 (3)	0.4703 (2)	0.8344 (2)	1.36 (11)
Zn(a)	0.1318 (2)	0.0817 (1)	0.0704 (1)	1.13 (6)
Cl(1a)	0.0881 (4)	0.0970 (2)	-0.0078 (2)	1.40 (11)
Cl(2a)	0.1589 (4)	0.1597 (2)	0.1141 (2)	1.28 (11)
Cl(3a)	0.0026 (3)	0.0456 (2)	0.1095 (2)	1.11 (11)
Cl(4a)	0.2467 (4)	0.0207 (2)	0.0808 (2)	2.08 (14)
Zn(b)	0.1396 (1)	0.0843 (1)	0.4028 (1)	0.73 (5)
Cl(1b)	0.1647 (4)	0.0938 (2)	0.3205 (2)	1.88 (13)
Cl(2b)	0.1469 (4)	0.1660 (2)	0.4434 (2)	1.87 (12)
Cl(3b)	0.0049 (4)	0.0466 (2)	0.4295 (2)	2.60 (14)
Cl(4b)	0.2553 (4)	0.0333 (2)	0.4384 (2)	2.14 (13)
Zn(c)	0.1206 (2)	0.0825 (1)	0.7400 (1)	0.95 (6)
Cl(1c)	0.1592 (4)	0.0902 (2)	0.6581 (2)	1.85 (13)
Cl(2c)	0.0952 (3)	0.1630 (2)	0.7806 (2)	1.06 (11)
Cl(3c)	0.0093 (4)	0.0219 (2)	0.7569 (2)	1.41 (12)
Cl(4c)	0.2563 (4)	0.0515 (2)	0.7778 (2)	1.47 (12)
Zn(d)	0.1181 (2)	0.4170 (1)	0.2413 (1)	0.94 (6)
Cl(1d)	0.1570 (4)	0.4065 (2)	0.1594 (2)	1.91 (13)
Cl(2d)	0.0799 (4)	0.3376 (2)	0.2810 (2)	1.37 (11)
Cl(3d)	0.0133 (4)	0.4820 (2)	0.2558 (2)	1.78 (13)
Cl(4d)	0.2557 (4)	0.4414 (2)	0.2804 (2)	1.78 (12)
Zn(e)	0.1288 (2)	0.4126 (1)	0.5723 (1)	0.91 (5)
Cl(1e)	0.0885 (4)	0.4012 (2)	0.4932 (2)	1.29 (11)
Cl(2e)	0.1688 (4)	0.3334 (2)	0.6129 (2)	1.68 (13)
Cl(3e)	-0.0005 (3)	0.4422 (2)	0.6130 (2)	1.61 (12)
Cl(4e)	0.2431 (4)	0.4740 (2)	0.5851 (2)	1.71 (12)
Zn(f)	0.1476 (2)	0.4170 (1)	0.9042 (1)	1.15 (6)
Cl(1f)	0.1663 (4)	0.4046 (2)	0.8214 (2)	1.81 (13)
Cl(2f)	0.1837 (4)	0.3379 (2)	0.9473 (2)	2.33 (14)
Cl(3f)	0.0047 (4)	0.4447 (2)	0.9290 (2)	2.26 (14)
Cl(4f)	0.2461 (4)	0.4823 (2)	0.9327 (2)	2.33 (14)
Zn(g)	0.3905 (2)	0.3327 (1)	0.0958 (1)	0.92 (5)
Cl(1g)	0.4207 (4)	0.3466 (2)	0.1766 (2)	1.68 (13)
Cl(2g)	0.4023 (4)	0.4119 (2)	0.0534 (2)	1.95 (13)
Cl(3g)	0.2544 (4)	0.2949 (2)	0.0779 (2)	1.89 (13)
Cl(4g)	0.4997 (4)	0.2753 (2)	0.0646 (2)	2.57 (15)
Zn(h)	0.3822 (2)	0.3316 (1)	0.4277 (1)	1.00 (5)
Cl(1h)	0.3374 (4)	0.3483 (2)	0.5092 (2)	1.49 (12)
Cl(2h)	0.4242 (4)	0.4082 (2)	0.3862 (2)	1.36 (12)
Cl(3h)	0.2492 (4)	0.3024 (2)	0.3884 (2)	1.96 (13)
Cl(4h)	0.4922 (4)	0.2671 (2)	0.4224 (2)	1.56 (12)
Zn(i)	0.3707 (2)	0.3355 (1)	0.7603 (1)	0.92 (5)
Cl(1i)	0.4105 (4)	0.3455 (2)	0.8412 (2)	1.86 (13)
Cl(2i)	0.3305 (4)	0.4140 (2)	0.7204 (2)	1.75 (13)
Cl(3i)	0.2610 (4)	0.2719 (2)	0.7478 (2)	1.61 (12)
Cl(4i)	0.5049 (4)	0.3098 (2)	0.7214 (2)	1.49 (12)
Zn(j)	0.3695 (2)	0.1686 (1)	0.2583 (1)	1.09 (6)
Cl(1j)	0.4036 (4)	0.1596 (2)	0.3396 (2)	1.74 (12)
Cl(2j)	0.3308 (4)	0.0897 (2)	0.2197 (2)	1.65 (13)
Cl(3j)	0.2602 (4)	0.2328 (2)	0.2435 (2)	1.84 (13)
Cl(4j)	0.5032 (4)	0.1966 (2)	0.2205 (2)	1.69 (13)
Zn(k)	0.3934 (2)	0.1662 (1)	0.5942 (1)	1.03 (6)
Cl(1k)	0.4023 (4)	0.1580 (2)	0.6773 (2)	1.42 (11)
Cl(2k)	0.4370 (4)	0.0869 (2)	0.5578 (2)	1.99 (13)
Cl(3k)	0.2543 (4)	0.1888 (2)	0.5637 (2)	1.91 (12)

† Coordinate fixed.

Table 1 (cont.)

	x	y	z	$U_{\text{eq}}$
Cl(4k)	0.4937 (4)	0.2323 (2)	0.5699 (2)	1.91 (13)
Zn(l)	0.3765 (2)	0.1624 (1)	0.9282 (1)	0.82 (5)
Cl(1l)	0.3373 (4)	0.1499 (2)	1.0110 (2)	1.44 (11)
Cl(2l)	0.4111 (4)	0.0834 (2)	0.8879 (2)	1.73 (13)
Cl(3l)	0.2437 (4)	0.1936 (2)	0.8908 (2)	1.59 (12)
Cl(4l)	0.4937 (4)	0.2211 (2)	0.9153 (2)	1.52 (12)

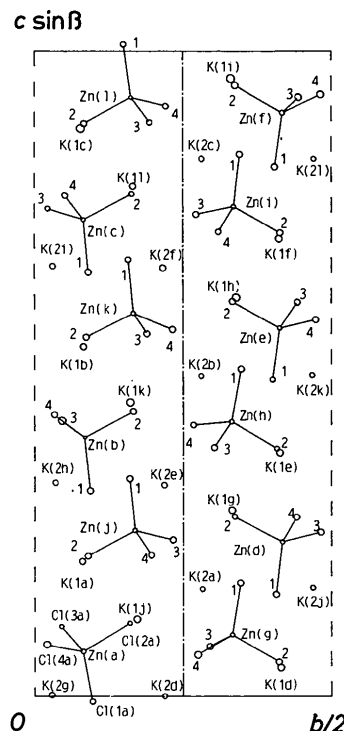


Fig. 1. Projection of the lower commensurate structure of  $\text{K}_2\text{ZnCl}_4$  at 140 K. Only independent atoms in one quarter of the unit cell are shown.

atoms along the  $a$  axis and by rotations of  $\text{ZnCl}_4$  tetrahedra about axes parallel to the  $c$  and  $b$  axes. The modulation period along the  $c$  axis is triple in the normal-phase structure. At room temperature the constituent atoms of the  $\text{Zn}(2)\text{--Cl}(5,6,7,8)$  tetrahedron in Mikahil & Peters (1979) have large thermal parameters. This and the other three tetrahedra which are symmetrically equivalent in the room-temperature phase are labeled as  $(b)$ ,  $(f)$ ,  $(g)$  and  $(k)$  in the structure of the low-temperature commensurate phase as seen in Fig. 1. These four tetrahedra deviate most from the corresponding positions in the room-temperature phase, shifting along the  $a$  axis and rotating about axes parallel to the  $c$  and  $b$  axes. Among them, the rotational displacements of  $(f)$  and  $(k)$  about the axis parallel to the  $c$  axis are most pronounced.

In Table 2, the mean cation-chlorine distances in  $\text{K}(1)$ ,  $\text{K}(2)$  and  $\text{Zn}$  polyhedra are listed. Distances

and angles of constituent atoms of the  $\text{ZnCl}_4$  tetrahedra averaged over all the equivalent bonds in the basic structure are also given. Each averaged tetrahedron is somehow distorted from the regular shape; for example, the averaged  $\text{Zn—Cl(1)}$  bond is shorter than  $\text{Zn—Cl(2)}$ , and the averaged  $\text{Cl(1)—Zn—Cl(2)}$  angle is larger than the others. These distortions are also recognized in the room-temperature structure. The mean  $\text{Zn—Cl}$  bond length and the mean  $\text{Cl—Zn—Cl}$  angle coincide with those of the room-temperature structure within their e.s.d.'s.

In an ideal  $\beta\text{-K}_2\text{SO}_4$ -type structure,  $\text{K(1)}$  is surrounded by eleven  $\text{Cl}$  atoms and  $\text{K(2)}$  by nine  $\text{Cl}$  atoms. In the structure of the low-temperature commensurate phase, as well as the room-temperature commensurate phase, six and eight  $\text{Cl}$  atoms are situated around  $\text{K(1)}$  and  $\text{K(2)}$ , respectively. The

Table 2. Mean cation–chlorine distances ( $\text{\AA}$ ) and  $\text{Cl—Zn—Cl}$  angles ( $^\circ$ ) of  $\text{K}_2\text{ZnCl}_4$  at 140 K

Site	$\text{K(1)—Cl}$	$\text{K(2)—Cl}$	$\text{Zn—Cl}$
(a)	3.168	3.223	2.257
(b)	3.278	3.193	2.266
(c)	3.286	3.272	2.274
(d)	3.262	3.206	2.273
(e)	3.235	3.246	2.256
(f)	3.165	3.260	2.271
(g)	3.196	3.200	2.240
(h)	3.238	3.229	2.279
(i)	3.263	3.268	2.261
(j)	3.262	3.251	2.258
(k)	3.290	3.196	2.246
(l)	3.204	3.234	2.278
Mean	3.237	3.231	2.263

$\text{Zn—Cl(1)}$	2.244	$\text{Cl(1)—Zn—Cl(2)}$	112.7
$\text{—Cl(2)}$	2.276	$\text{Cl(1)—Zn—Cl(3)}$	112.0
$\text{—Cl(3)}$	2.260	$\text{Cl(1)—Zn—Cl(4)}$	109.5
$\text{—Cl(4)}$	2.272	$\text{Cl(2)—Zn—Cl(3)}$	107.6
Mean	2.263	$\text{Cl(2)—Zn—Cl(4)}$	106.8
		$\text{Cl(3)—Zn—Cl(4)}$	107.6
		Mean	109.4

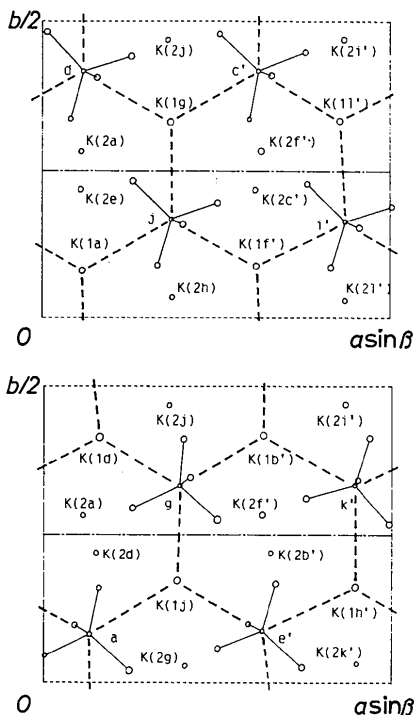


Fig. 2. Projections along the  $c$  axis. The bottom is for  $0 < z < \frac{1}{6}$  and the top for  $\frac{1}{6} < z < \frac{1}{3}$ . Pseudo-hexagonal networks are indicated by broken lines. Symmetry code for primed atoms is  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .

mean  $\text{K(1)—Cl}$  and  $\text{K(2)—Cl}$  distances are 3.305 and 3.258  $\text{\AA}$  at room temperature (Mikhail & Peters, 1979). In the low-temperature phase, the former distance shrinks by 1.9% and the latter by 0.8%. The cell dimensions decrease by 0.8% of those at room temperature. Therefore the shortening of the  $\text{K(1)—Cl}$  distance is notable.

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#### References

- CUMMINS, H. Z. (1990). *Phys. Rep.* **185**, 211–411.  
 GESI, K. (1978). *J. Phys. Soc. Jpn.* **45**, 1438–1439.  
 GESI, K. (1990). *J. Phys. Soc. Jpn.* **59**, 416–419.  
 GESI, K. & IIZUMI, M. (1979). *J. Phys. Soc. Jpn.* **46**, 697–698.  
 HASEBE, K. (1990). Private communication.  
 IIZUMI, M., AXE, J. D., SHIRANE, G. & SHIMAOKA, K. (1977). *Phys. Rev. B*, **15**, 4392–4411.  
 MASHIYAMA, H. (1991). *J. Phys. Soc. Jpn.* **60**, 180–187.  
 MIKHAIL, I. & PETERS, K. (1979). *Acta Cryst.* **B35**, 1200–1201.  
 MILLIA, F., KIND, R. & SLAK, J. (1983). *Phys. Rev. B*, **27**, 6662–6668.  
 QUILCHINI, M., BERNEDE, P., LEFEBVRE, J. & SCHWEISS, P. (1990). *J. Phys. Condens. Matter*, **2**, 4543–4558.  
 SEKINE, T., TAKAYAMA, M., UCHINOKURA, K. & MATSUURA, E. (1986). *J. Phys. Soc. Jpn.* **55**, 3903–3917.  
 WYCKOFF, R. W. G. (1965). *Crystal Structures*, 2nd ed. Vol. III, ch. VIII, b.11. New York: John Wiley.