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Lists of experimental data, refinement parameters and primary diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55807 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1018]

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## Structure Determination of $K_2ZnBr_4$ at 291 and 144 K

J. FÁBRY,\*† T. BREZEWSKI‡ AND F. J. ZÚÑIGA

*Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain*

A. R. ARNAIZ

*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain*

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## Abstract

The room-temperature phase of  $K_2ZnBr_4$  is isomorphous with  $Sr_2GeS_4$  ( $P2_1/m$ ) while the low-temperature structure ( $P2_1$ ) is slightly distorted [the phase transition occurs at 155 K]. Both structures con-

tain highly deformed tetrahedral  $[ZnBr_4]^{2-}$  molecules with  $Br(3)-Zn-Br(3')$  angles of 103.06 (5) and 102.49 (9)° at 291 and 144 K, respectively. This distortion is caused by the repulsion of Br atoms whose distance 3.712 (1) and 3.661 (2) Å at 291 and 144 K, respectively, is below the Br—Br van der Waals distance (3.9 Å). The phase transition is accompanied by minor shifts of cations and  $[ZnBr_4]^{2-}$  tetrahedra which are simultaneously rotated about a small angle. Below the phase transition point an inversion twin develops whose twinning parameter was refined to 0.459 (65).

## Comment

Among compounds of composition  $A_2BX_4$  two families exist. The first contains structures which are isomorphous with  $\beta-K_2SO_4$  and which typically exhibit phase-transition sequences (e.g. on decreasing temperature), from the prototype  $\beta-K_2SO_4$  to an incommensurate structure which is followed by a transition to the lock-in ferroelectric phase. The other family is related to  $Sr_2GeS_4$ ; either isomorphous with it ( $P2_1/m$ ) or slightly distorted ( $P2_1$ ). At lower temperatures transitions to a ferroelectric state sometimes occur:  $Rb_2ZnI_4$ ,  $Tl_2ZnI_4$  (Gesi, 1984),  $K_2ZnBr_4$  (Shimizu, Yamaguchi, Suzuki, Takashige & Sawada, 1990) and  $K_2CoBr_4$  (Suzuki, Shimizu, Takashige, Sawada & Yamaguchi, 1990). The latter three structures are reported to undergo a  $P2_1/m \rightarrow P2_1$  phase transition (Gesi, 1984; Ammlung, Scaringe, Ibers, Shriver & Whitmore, 1979; Mashiyama, Kasano & Yamaguchi, 1991).

On the other hand, there are some rare cases where the  $Sr_2GeS_4$  isomorphs transform when heated to the  $\beta-K_2SO_4$  structure, e.g.  $Tl_2CoBr_4$ ,  $K_2CoBr_4$  (Seifert & Stäudel, 1977) and  $Cs_2CdI_4$  (Touchard, Louër, Auffredic & Louër, 1987).

Phase transitions in  $K_2CoBr_4$  (Suzuki, Shimizu, Takashige, Sawada & Yamaguchi, 1990) and  $K_2ZnBr_4$  (Shimizu, Yamaguchi, Suzuki, Takashige & Sawada, 1990) have recently been studied by dielectric measurements and DTA (differential thermal analysis). These experiments revealed similar behaviour in both compounds and showed the existence of a ferroelectric phase below 143 and 155 K for  $K_2CoBr_4$  and  $K_2ZnBr_4$ , respectively. Mashiyama, Kasano & Yamaguchi (1991) determined their space groups and discovered the existence of an incommensurate phase [ $q = (1/3 - \delta)c^*$ ] of the basic  $\beta-K_2SO_4$  structure isomorphs ( $Pm\bar{c}n$ ) in the region 473–555 and 473–561 K for  $K_2CoBr_4$  and  $K_2ZnBr_4$ , respectively. Above these temperature intervals unmodulated phases of the prototype  $\beta-K_2SO_4$  structure exist. When the incommensurate phases are quickly supercooled the commensurate threefold structures appear. These are, however, thermodynamically

† Currently at the Institute of Physics of the Czechoslovak Academy of Sciences, Cukrovarnicka 10, 162 00 Praha 6, Czechoslovakia.

‡ On leave of absence from the Institute of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland.

unstable with regard to  $\text{Sr}_2\text{GeS}_4$  isomorphs ( $\alpha$ -phases). The ability of  $\text{K}_2\text{CoBr}_4$  and  $\text{K}_2\text{ZnBr}_4$  to appear in modifications which are related to  $\text{Sr}_2\text{GeS}_4$  and  $\beta\text{-K}_2\text{SO}_4$  structure types makes their structure determination of interest. This work deals with the X-ray structure determination of the monoclinic  $\text{K}_2\text{ZnBr}_4$  at 291 and 144 K.

The coordinates of  $\text{Rb}_2\text{CoI}_4$  (Seifert & Stäudel, 1977) were used as a starting model for the refinement of the high-temperature structure. The phase transition to the low-temperature phase may be accompanied by development of an inversion-twinned crystal.

Following Flack (1983) the twin-fraction parameter  $x$  of an inversion-twinned crystal may be expressed as:

$$|F_o[\mathbf{h},(1-x)]|^2 = (1-x)|F(\mathbf{h})|^2 + x|F(-\mathbf{h})|^2 \quad (1)$$

where  $|F_o[\mathbf{h},(1-x)]|$  corresponds to the square root of observed intensity (corrected for Lp factor, absorption and fluctuation of checking reflections) of a reflection  $\mathbf{h}$  diffracted by an inversion-twinned crystal.

Following (1) the difference Fourier synthesis  $\Delta\rho = V^{-1}\sum_n \Delta F(\mathbf{h})e^{-2\pi i\mathbf{h}\cdot\mathbf{r}}$ , where  $\Delta F(\mathbf{h}) = |F_o(\mathbf{h})/Sc - |F_c(\mathbf{h})|$  for a non-twinned case ( $Sc$  is a general scale factor), is modified for an inversion-twinned crystal:

$$\Delta F(\mathbf{h}) = \left[ \frac{\left\{ \frac{F_o[\mathbf{h},(1-x)]}{Sc} \right\}^2 - x|F_c(-\mathbf{h})|^2}{(1-x)} \right]^{1/2} - |F_c(\mathbf{h})|, \quad x \neq 1.$$

The modified difference Fourier synthesis which was calculated for  $x = 0.5$   $\{F_o[\mathbf{h},(1-x)]$  were determined from reflection intensities of the low-temperature phase while  $F_c(\mathbf{h})$  from the model of the high-temperature phase} revealed positions of the shifted Br atoms of the low-temperature phase. The Br(2) atom was split into two positions which were related by inversion. {This splitting of the Br(2) atom was also observed in the difference Fourier map when no twinning was included [ $\Delta F(\mathbf{h}) = |F_o(\mathbf{h})/Sc - |F_c(\mathbf{h})|$ ].} Refinement [ $y$  coordinate of Br(3) atom fixed] of the two models which differed in the choice of the Br(2) atom converged to virtually the same minimum: the atomic positions of the respective models were linked by inversion and the twin-fraction values were interchanged.

The refinement without introducing the twin-fraction parameter gave a worse result both for the inverted and non-inverted structure models [ $R(x=1) = 0.0499$ ,  $wR(x=1) = 0.0610$ ,  $S(x=1) = 1.348$ ,  $R(x=0) = 0.0502$ ,  $wR(x=0) = 0.0608$ ,  $S(x=0) = 1.339$ ;  $R$  factors apply for reflections  $I > 3\sigma(I)$ ].

The most interesting feature of both phases is the presence of the extremely distorted  $[\text{ZnBr}_4]^{2-}$  molecule which is more distorted than that observed in

$[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$  (Asahi, Hasebe & Gesi, 1988) and  $\text{Rb}_2\text{ZnBr}_4$  (de Pater, 1979).

In  $\text{Rb}_2\text{ZnBr}_4$ , the Zn—Br bond lengths lie between 2.37–2.39 Å and the Br—Zn—Br bond angles between 106–114°. In  $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$  the bond lengths are between 2.36–2.45 Å and the bond angles between 106.7–112.4°. The deformation of  $[\text{ZnBr}_4]^{2-}$  in the present structure may be explained by the repulsion of Br(3) atoms from the neighbouring tetrahedra. The intermolecular distances Br(3)—Br(3')/Br(3A) are 3.712 (1) and 3.661 (2) Å for 291 and 144 K, respectively, being substantially below the Br—Br van der Waals distance [ $r_{\text{vdW}}(\text{Br}) = 1.95$  Å; Bondi (1964)] and somewhat shorter than the intramolecular distances 3.765 (1) Å (291 K) and 3.756 (2) Å (144 K) between the Br atoms of the same species. These Br atoms subtend an extremely small angle at Zn: Br(3)—Zn—Br(3') = 103.06 (5)° (291 K) and Br(3)—Zn—Br(3A) = 102.49 (9)° (144 K). It is worth noting the much smaller  $U_{22}$  component of the thermal factor of Br(3)/Br(3A) atoms in comparison with Br(1) and Br(2). This seems to be related to the close contacts between these Br atoms along the  $b$  axis. It is also interesting that although the volume of the unit cell decreases, the length of the  $b$  axis somewhat increases during the  $P2_1/m \rightarrow P2_1$  phase transition.

Table 3 lists structures related to the  $\text{Sr}_2\text{GeS}_4$  structure type (Bergerhoff, Hundt, Sievers & Brown, 1983). It can be seen that all these structures contain highly deformed tetrahedral molecules. All the isostructural compounds reported by Gesi (1984)

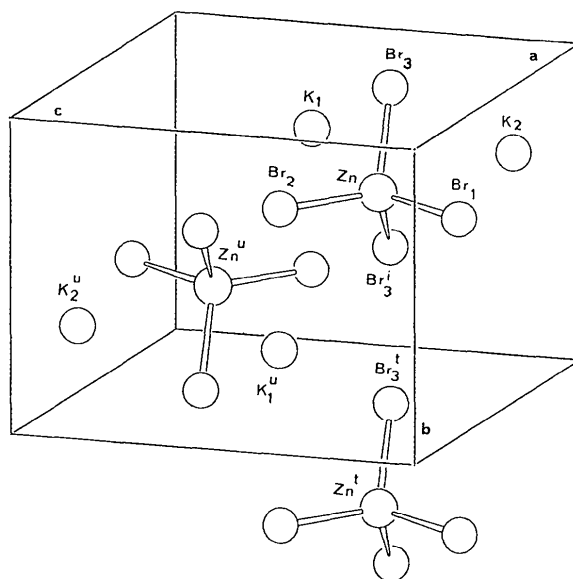


Fig. 1. View of the unit cell of  $\text{K}_2\text{ZnBr}_4$  at 291 K.  $\text{Zn}^u$  and  $\text{Br}^i$  are translation equivalents of Zn and Br atoms, respectively. The non-primed and  $u$ -primed atoms and molecules are linked by inversion ( $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$ ).

and Zandbergen, Verschoor & IJdo (1979) are complex iodides or bromides; *i.e.* they contain polarizable and deformable anions.

The present structure is the first one among these isostructural compounds where inversion twinning was observed.  $\text{Rb}_2\text{FeI}_4$  (Zandbergen, Verschoor & IJdo, 1979) was suspected to be another candidate where inversion twinning could have appeared. The authors could not distinguish between the inverted structure models because refinement converged to the same values of  $R$  factors. The refinement of  $\text{Rb}_2\text{FeI}_4$  which included the twin-fraction parameter ( $w = 1$ ) [Zandbergen, Verschoor & IJdo (1979), Supplementary Publication No. SUP 34273]. This refinement, however, did not give a decisive answer about whether inversion twinning takes place in this compound:  $x = 0$ ,  $R = 0.0418$ ,  $wR = 0.0444$ ;  $x = 1$ ,  $R = 0.0419$ ,  $wR = 0.0442$ ;  $x = 0.27$  (26),  $R = 0.0417$ ,  $wR = 0.0442$ . The reflection set from the supplementary material contained, however, only independent reflections from 1/4 of the reciprocal space (with the exception of 112 and  $\bar{1}\bar{1}\bar{2}$  reflections).

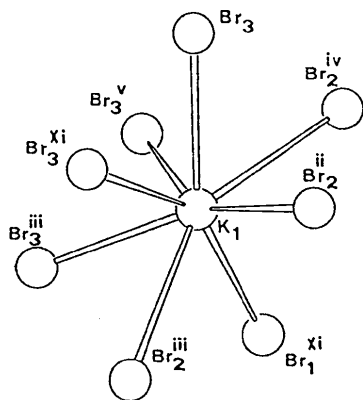


Fig. 2. Environment of K(1) atom.

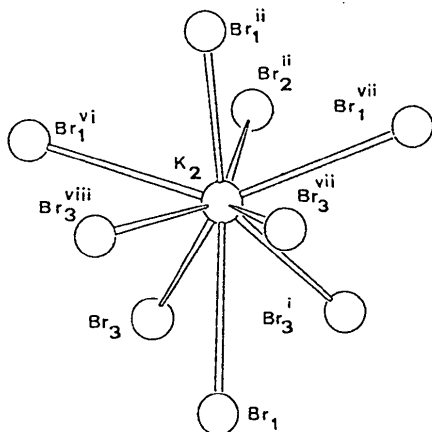


Fig. 3. Environment of K(2) atom.

## Experimental

### At 291 K

#### Crystal data

$\text{K}_2\text{ZnBr}_4$   
 $M_r = 463.19$   
 Monoclinic  
 $P2_1/m$   
 $a = 7.200$  (2) Å  
 $b = 7.477$  (2) Å  
 $c = 9.144$  (3) Å  
 $\beta = 108.95$  (1)°  
 $V = 465.3$  Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 3.303$  Mg m<sup>-3</sup>

#### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega$  scans  
 Absorption correction:  
 spherical  
 $T_{\min} = 0.0362$ ,  $T_{\max} = 0.0551$   
 3393 measured reflections  
 881 independent reflections  
 533 observed reflections  
 $[I \geq 3\sigma(I)]$

#### Refinement

Refinement on  $F$   
 Final  $R = 0.0282$   
 $wR = 0.0315$   
 $S = 1.123$   
 533 reflections  
 40 parameters  
 $w = [\sigma^2(F_o) + (0.01|F_o|)^2]^{-1}$   
 $(\Delta/\sigma)_{\max} = 0.01$

### At 144 K

#### Crystal data

$\text{K}_2\text{ZnBr}_4$   
 $M_r = 463.19$   
 Monoclinic  
 $P2_1$   
 $a = 7.204$  (3) Å  
 $b = 7.413$  (4) Å  
 $c = 9.028$  (5) Å  
 $\beta = 108.67$  (3)°  
 $V = 456.7$  (6) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 3.367$  Mg m<sup>-3</sup>

Cu  $K\alpha_1$  radiation for powder  
 diffraction  
 $\lambda = 1.54056$  Å  
 Mo  $K\alpha$  radiation for single  
 crystal  
 $\lambda = 0.71073$  Å  
 $\theta = 5-23.75^\circ$   
 $\mu = 2.052$  mm<sup>-1</sup>  
 $T = 291$  (1) K  
 0.128 (8) mm (radius)  
 Colourless  
 Crystal source: prepared by  
 the Bridgman method

$R_{\text{int}} = 0.047$   
 $\theta_{\max} = 25^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -8 \rightarrow 8$   
 $l = -10 \rightarrow 10$   
 4 standard reflections  
 frequency: 60 min  
 intensity variation:  
 <5%

$\Delta\rho_{\max} = 1.27$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.05$  e Å<sup>-3</sup>  
 Atomic scattering factors  
 from Cromer & Mann  
 (1968) and *International  
 Tables for X-ray Crystal-  
 lography* (1974, Vol. IV)

Cu  $K\alpha_1$  radiation for powder  
 diffraction  
 $\lambda = 1.54056$  Å  
 Mo  $K\alpha$  radiation for single  
 crystal  
 $\lambda = 0.71073$  Å  
 $\theta = 5-25^\circ$   
 $\mu = 2.092$  mm<sup>-1</sup>  
 $T = 144$  (3) K  
 0.128(8) mm (radius)  
 Colourless  
 Crystal source: prepared by  
 the Bridgman method

Table 1. Atomic positional parameters and anisotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) with e.s.d.'s in parentheses

The anisotropic temperature factors are of the form:  
 $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
K(1)*	0.7809 (4)	0.2500	0.5744 (3)	603 (18)	819 (24)	435 (16)	—	220 (14)	—
	0.7748 (5)	0.245 (1)	0.5726 (4)	334 (16)	499 (25)	214 (15)	32 (32)	93 (13)	-2 (31)
K(2)	0.7043 (4)	0.2500	0.0440 (3)	537 (18)	806 (23)	432 (15)	—	173 (13)	—
	0.7087 (5)	0.245 (1)	0.0467 (4)	316 (16)	521 (26)	203 (14)	6 (31)	68 (12)	102 (30)
Zn	0.2816 (2)	0.2500	0.2066 (1)	385 (8)	455 (9)	428 (7)	—	164 (6)	—
	0.2804 (2)	0.2573 (6)	0.2050 (2)	243 (8)	294 (8)	220 (7)	16 (15)	80 (6)	27 (15)
Br(1)	0.1073 (2)	0.2500	-0.0656 (1)	581 (9)	1117 (14)	377 (7)	—	140 (6)	—
	0.1029 (2)	0.2691 (6)	-0.0693 (2)	333 (8)	679 (14)	190 (7)	-54 (16)	48 (6)	-15 (15)
Br(2)	0.0750 (2)	0.2500	0.3635 (1)	460 (8)	1284 (14)	445 (7)	—	225 (6)	—
	0.0769 (2)	0.2656 (7)	0.3676 (2)	259 (7)	781 (13)	229 (7)	-78 (17)	97 (6)	-44 (17)
Br(3)	0.5012 (1)	-0.0018 (1)	0.2667 (1)	548 (5)	376 (4)	572 (5)	40 (4)	185 (4)	10 (5)
	0.4929 (4)	-0.001786†	0.2618 (3)	378 (14)	289 (13)	323 (15)	64 (12)	72 (11)	14 (12)
Br(3A)	—	—	—	—	—	—	—	—	—
	0.5093 (4)	0.5046 (3)	0.2681 (3)	270 (11)	200 (11)	257 (13)	30 (10)	77 (9)	5 (10)

\* First row: structure at 291 K; second row: phase at 144 K.

† Fixed coordinate.

### Data collection

Enraf-Nonius CAD-4 diffractometer

 $\omega$  scans

Absorption correction: spherical

 $T_{\min} = 0.0360$ ,  $T_{\max} = 0.0549$ 

1696 measured reflections

1594 independent reflections

1141 observed reflections

 $[I \geq 3\sigma(I)]$  $R_{\text{int}} = 0.039$  $\theta_{\max} = 25^\circ$  $h = -8 \rightarrow 8$  $k = -8 \rightarrow 8$  $l = 0 \rightarrow 10$ 

4 standard reflections

frequency: 60 min

intensity variation:

&lt;7%

### Refinement

Refinement on  $F$ Final  $R = 0.0493$  $wR = 0.0597$  $S = 1.318$ 

1141 reflections

64 parameters

 $w = [\sigma^2(F_o) + (0.03|F_o|^2)]^{-1}$  $(\Delta/\sigma)_{\max} = 0.01$  $\Delta\rho_{\max} = 4.06 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -4.16 \text{ e \AA}^{-3}$ 

Atomic scattering factors

from Cromer &amp; Mann

(1968) and *International**Tables for X-ray Crystal-**lography* (1974, Vol. IV)

The crystals are soft and extremely hygroscopic and all manipulations were performed in a dry nitrogen atmosphere or in cyclohexane. The single crystal was prepared by grinding which turned out to be the only feasible way of obtaining a sample of well defined shape with non-split reflection profiles. The grinding, however, caused the reflection profiles to be very broad and consequently the accuracy of the lattice parameters obtained from the single crystal was inferior to that obtained from the powder experiment. Thus the result of the powder diffraction experiment for the determination of cell parameters is reported here. These experiments were performed on a Stoe focusing monochromatic transmission diffractometer equipped with a linear position detector. The powdered sample was inserted into a Lindemann-glass capillary of 0.3 mm diameter. The lattice parameters at 158(3) K are:  $a = 7.214(3)$ ,  $b = 7.378(4)$ ,  $c = 9.063(3)$  \AA,  $\beta = 108.53(3)^\circ$ ,  $V = 457.4(5)$  \AA<sup>3</sup>. The measured region was 5 - 25° for the structure at 158 K. Figures of merit

$F[N_{\text{obs}}/(\Delta 2\theta)_{\text{average}}]$  after least-squares refinement of lattice parameters are:  $F(18/0.007) = 34.75$  for 144 K,  $F(14/0.007) = 22.99$  for 158 K and  $F(20/0.006) = 37.05$  for 291 K. The temperature stabilities of the single-crystal and powder experiments were  $\pm 1$  and  $\pm 3$  K, respectively.

In the determination at 144 K, the refinement indicated that the phase transition from  $P2_1/m$  to  $P2_1$  was accompanied by the formation of the inversion-twinned crystal with a domain fraction parameter which was refined to 0.459(65).

The program used for the powder diffraction experiment was *STADI P* (Stoe & Cie, 1987). The program used for structure solution and refinement was the *SDS* (Petříček & Malý, 1988) system. Figs. 1, 2 and 3 were prepared using *SCHAKAL88* (Keller, 1989). Table 1 lists atomic coordinates and anisotropic thermal parameters and Table 2 lists selected interatomic distances and angles.

Table 2. Selected interatomic distances (\AA) and angles (°)

	291 K	144 K
Zn—Br(1)/Br(1)	2.396 (2)	2.398 (2)
Zn—Br(2)/Br(2)	2.378 (2)	2.385 (3)
Zn—Br(3)/Br(3)	2.405 (1)	2.407 (4)
Zn—Br(3 <sup>ii</sup> )/Br(3A)	2.405 (1)	2.410 (4)
K(1)—Br(1 <sup>ii</sup> )/Br(1 <sup>ii</sup> )	3.366 (3)	3.343 (3)
K(1)—Br(2 <sup>ii</sup> )/Br(2 <sup>ii</sup> )	3.295 (4)	3.281 (4)
K(1)—Br(2 <sup>iii</sup> )/Br(2 <sup>iii</sup> )	3.872 (1)	3.703 (10)
K(1)—Br(2 <sup>iiii</sup> )/Br(2 <sup>iiii</sup> )	3.872 (1)	3.992 (10)
K(1)—Br(3 <sup>i</sup> )/Br(3A <sup>ii</sup> )	3.406 (3)	3.366 (6)
K(1)—Br(3 <sup>iii</sup> )/Br(3 <sup>iii</sup> )	3.406 (3)	3.364 (6)
K(1)—Br(3 <sup>iv</sup> )/Br(3A)	3.441 (2)	3.398 (6)
K(1)—Br(3)/Br(3)	3.441 (2)	3.421 (6)
K(2)—Br(1 <sup>ii</sup> )/Br(1 <sup>ii</sup> )	3.364 (4)	3.332 (4)
K(2)—Br(1 <sup>iii</sup> )/Br(1 <sup>iii</sup> )	3.960 (1)	3.765 (9)
K(2)—Br(1 <sup>iv</sup> )/Br(1 <sup>iv</sup> )	3.960 (1)	4.096 (9)
K(2)—Br(1)/Br(1)	4.084 (3)	4.153 (4)
K(2)—Br(2 <sup>ii</sup> )/Br(2 <sup>ii</sup> )	3.255 (3)	3.245 (3)
K(2)—Br(3)/Br(3)	3.430 (3)	3.388 (6)
K(2)—Br(3 <sup>ii</sup> )/Br(3A)	3.430 (3)	3.404 (6)
K(2)—Br(3 <sup>iii</sup> )/Br(3 <sup>iii</sup> )	3.313 (2)	3.285 (6)
K(2)—Br(3 <sup>iiii</sup> )/Br(3A <sup>ii</sup> )	3.313 (2)	3.298 (6)
Br(1)—Br(2)/Br(2)	4.006 (2)	4.009 (2)
Br(1)—Br(3)/Br(3)	3.902 (1)	3.935 (3)
Br(1)—Br(3 <sup>i</sup> )/Br(3A)	3.902 (1)	3.897 (3)

Br(2)—Br(3)/Br(3)	3.938 (2)	3.957 (4)
Br(2)—Br(3 <sup>h</sup> )/Br(3A)	3.938 (2)	3.930 (4)
Br(3)—Br(3 <sup>h</sup> )/Br(3A <sup>h</sup> )	3.712 (1)*	3.661 (2)*
Br(3)—Br(3 <sup>h</sup> )/Br(3A)	3.765 (1)	3.756 (2)
Br(1)—Zn—Br(2)	114.06 (7)	113.91 (8)
Br(1)—Zn—Br(3 <sup>h</sup> )/Br(3)	108.72 (5)	110.0 (2)
Br(1)—Zn—Br(3 <sup>h</sup> )/Br(3A)	108.72 (5)	108.3 (2)
Br(2)—Zn—Br(3)	110.84 (5)	111.3 (2)
Br(2)—Zn—Br(3 <sup>h</sup> )/Br(3A)	110.84 (5)	110.1 (2)
Br(3)—Zn—Br(3 <sup>h</sup> )/Br(3A)	103.06 (5)	102.49 (9)

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

\* Denotes intermolecular distance.

Table 3.  $A_2[BX_4]$  structures related to the  $Sr_2GeS_4$  structure type

Space group	R	Shortest X—X intra-/intermolecular distance (Å)		Minimal/maximal angle (°) within $[BX_4]$	T(K)*
		in $[BX_4]$			
Ba <sub>2</sub> SiSe <sub>4</sub> <sup>a</sup>	$P2_1/m$	0.071	3.577 (2)/3.456 (2)	105.3 (3)/116.3 (3)	
Ba <sub>2</sub> SiTe <sub>4</sub> <sup>a</sup>	$P2_1/m$	0.059	3.917 (1)/3.709 (1)	103.5 (2)/117.9 (2)	
Cs <sub>2</sub> CdI <sub>4</sub> <sup>b</sup>	$P2_1/m$	0.029	4.3980 (5)/3.9990 (5)	105.50 (4)/113.93 (4)	
Cs <sub>2</sub> HgI <sub>4</sub> <sup>c</sup>	$P2_1/m$	0.032	4.4402 (7)/3.9458 (7)	106.35 (3)/114.03 (3)	
Eu <sub>2</sub> GeS <sub>4</sub> <sup>d</sup>	$P2_1$	0.032	3.389 (9)/3.288 (9)	100.9 (2)/115.2 (2)	
K <sub>2</sub> ZnBr <sub>4</sub> <sup>e</sup>	$P2_1/m$	0.028	3.765 (1)/3.712 (1)	103.06 (5)/114.06 (7)	
K <sub>2</sub> ZnBr <sub>4</sub> <sup>e</sup>	$P2_1$	0.049	3.756 (2)/3.661 (2)	102.49 (9)/113.91 (8)	144
Rb <sub>2</sub> CoI <sub>4</sub> <sup>f</sup>	$P2_1/m$	0.150	4.137 (4)/4.007 (4)	106.0 (2)/114.2 (2)	
Rb <sub>2</sub> FeI <sub>4</sub> <sup>f</sup>	$P2_1$	0.041	4.152 (3)/4.032 (3)	103.96 (9)/115.91 (6)	
Sr <sub>2</sub> GeS <sub>4</sub> <sup>g</sup>	$P2_1/m$	0.096	3.402 (6)/3.327 (6)	101.5 (2)/115.7 (2)	
Tl <sub>2</sub> ZnI <sub>4</sub> <sup>i</sup>	$P2_1$	0.120	4.090 (15)/3.919 (15)	101.8 (10)/114.0 (10)	113

References: (a) Brinkmann, Eisenmann & Schaefer (1985); (b) Sjövall (1989); (c) Sjövall & Svensson (1988); (d) Bugli, Dugue & Barnier (1979); (e) This work; (f) Seifert & Stäudel (1977); (g) Zandbergen, Verschoor & IJdo (1979); (h) Philippot, Ribes & Maurin (1971); (i) Ammlung, Scaringe, Ibers, Shriver & Whitmore (1979).

\* If temperature is not specified the structure is assumed to have been measured at room temperature.

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Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55884 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL9484]

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## Structure de K<sub>8</sub>Th(MoO<sub>4</sub>)<sub>6</sub>

M. HUYGHE, M.-R. LEE, S. JAULMES ET M. QUARTON

Laboratoire de Cristallographie du Solide,  
 URA 1388 du CNRS, Université Pierre et Marie Curie,  
 4 place Jussieu, 75252 Paris CEDEX 05, France

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## Abstract

The cation array in the compound, octapotassium thorium hexamolybdate, is very similar to that of palmierite-like  $K_2Pb(SO_4)_2$ ;  $K_8(K_2Th)(MoO_4)_6$  is equivalent to  $3K_2Pb(SO_4)_2$ . Three atoms (K, K, Th) are found to be ordered over the Pb sites along some particular directions. The triclinic cell is related to the  $K_2Pb(SO_4)_2$  hexagonal one by  $a_t = a_h - b_h$ ,  $b_t = a_h + 2b_h$  and  $c_t = 2c_h/3$ . The structure consists of two different densely packed layers. In contrast to the palmierite, the K—O distances have a wide range of values whereas the Th atom exhibits an eightfold coordination with bond lengths ranging from 2.31 to 2.56 Å.