

Computer programs utilized include *SHELXS86* (Sheldrick, 1990) for structure solution, *SHELX76* (Sheldrick, 1976) for structure refinement, *ORTEP* (Johnson, 1976) for the preparation of Fig. 1 and *SYBYL* (Tripos Associates, 1993) for the preparation of Fig. 2.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: BR1061). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Hexagonal $\text{Yb}_6\text{Cr}_{4+x}\text{Al}_{43-x}$ ( $x = 1.76$ ) with a New Structure Type

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## Abstract

The title compound contains one Yb, two Cr and seven Al sites, one of which is about half occupied by Cr. The coordination polyhedron of Yb has 17 vertices and composition  $[\text{Cr}(\text{Al}, \text{Cr})_2\text{Al}_{13}\text{Yb}]$ , while those around Cr are  $[\text{Al}_{10}\text{Yb}_2]$  and  $[\text{Al}_{12}]$ , and that around the mixed site is  $[\text{Al}_9\text{Yb}_3]$ .

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## Comment

Aluminium-rich rare-earth (*R*) transition-metal (*T*) compounds of approximate composition  $RT\text{Al}_8$  are known for  $R = \text{Y}, \text{Dy}, \text{Sm}, \text{Tb}$  and  $T = \text{V}, \text{Cr}$  (Zarechnyuk, Rykhal' & German, 1971; Rykhal', Zarechnyuk & Mats'kiv, 1979; Zarechnyuk, Yanson, Ostrovskaya & Shevchuk, 1988). Investigation of the system  $\text{Yb}-\text{Cr}-\text{Al}$  at 773 K revealed the existence of a similar compound.

The structure of  $\text{Yb}_6\text{Cr}_{4+x}\text{Al}_{43-x}$  is of a new type. It contains one Yb, two Cr and seven Al sites, one of which is occupied partially by Cr (Fig. 1). The coordination polyhedron of Yb has 17 vertices and composition  $[\text{Cr}(\text{Al}, \text{Cr})_2\text{Al}_{13}\text{Yb}]$ . The polyhedra of the two ordered chromium sites Cr(1) and Cr(2), and the disordered metal site Al(6) ( $\equiv \text{Al}_{0.56}\text{Cr}_{0.44}$ ) each have 12 vertices; their compositions are  $[\text{Al}_{10}\text{Yb}_2]$ ,  $[\text{Al}_{12}]$  and  $[\text{Al}_9\text{Yb}_3]$ , respectively. The polyhedra around Cr(1) and Al(6) each have a deformed icosahedral shape, while that around Cr(2) has a regular icosahedral shape, as in many other Al-rich transition-metal compounds (Kripyakevich, 1977). The polyhedra around the other six Al sites all each have 12 vertices and are deformed icosahedra or bicapped pentagonal prisms  $[\text{Al}(7)]$ . The polyhedra around the Cr(1) sites are linked parallel to the hexagonal plane in groups of three *via* common Al atoms and these units are linked perpendicular to the hexagonal plane to form columns along  $[001]$  at  $x = 0, y = 0$  *via* Cr(2) icosahedra (Fig. 2). Adjacent columns are connected *via* interpenetrated Al(6) and Yb polyhedra. All other Al polyhedra interpenetrate with Cr(1), Cr(2), Al(6) or Yb polyhedra. The architecture of the columns of Cr polyhedra (without the Yb atoms) resembles that of hexagonal  $\text{V}_4\text{Al}_{23}$  (Smith & Ray, 1957). This structure also contains two transition-metal sites. One of these is icosahedrally coordinated with Al atoms [as in

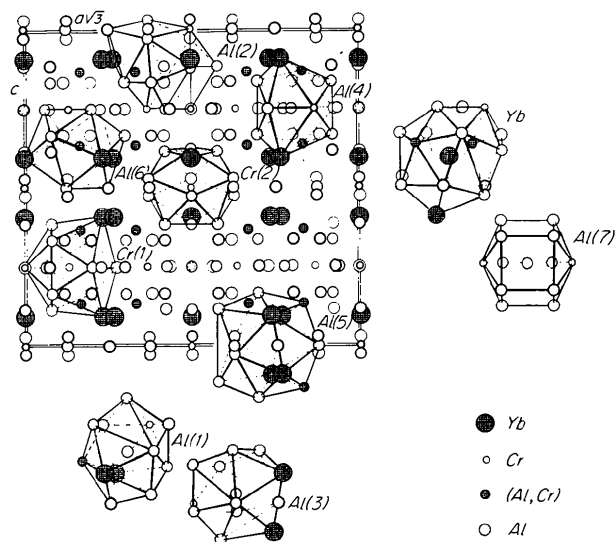


Fig. 1. Structural projection of hexagonal  $\text{Yb}_6\text{Cr}_{4+x}\text{Al}_{43-x}$  along  $[010]$  showing the coordination polyhedra.

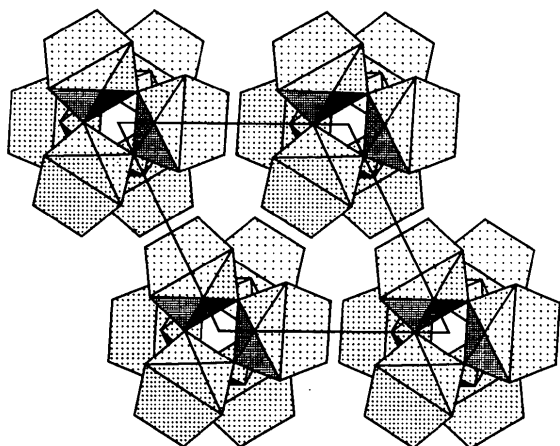
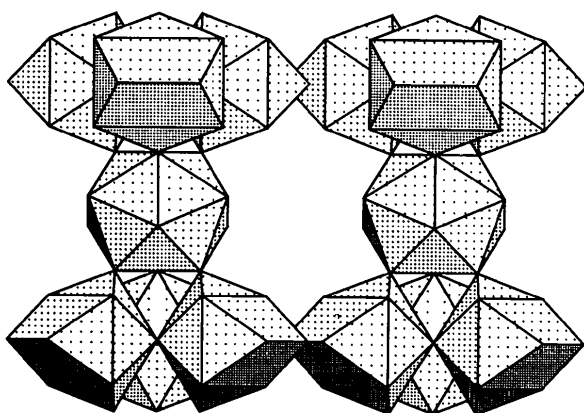
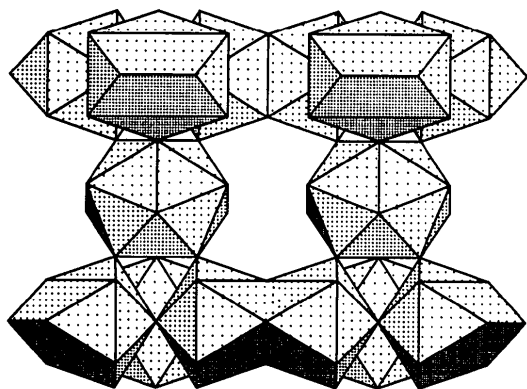


Fig. 2. Coordination polyhedra around Cr(1) (without the two Yb atoms) and Cr(2) in Yb<sub>6</sub>Cr<sub>4+x</sub>Al<sub>43-x</sub> viewed along the [001] direction. The Cr(2) icosahedra are positioned on the plane  $z = 0$ .



(a)



(b)

Fig. 3. Coordination polyhedra around (a) Cr(1) (without the two Yb atoms) and Cr(2) in Yb<sub>6</sub>Cr<sub>4+x</sub>Al<sub>43-x</sub> viewed along the [100] direction and (b) around both V sites in V<sub>4</sub>Al<sub>23</sub> viewed along the [310] direction. The Cr(2) and V icosahedra are positioned on the plane  $z = 0$ .

Cr(2) in the present compound], while the other has eight Al and two V neighbours, thus forming polyhedra which are of the same shape as those of Cr(1) without the two Yb atoms (Schubert, 1964). These polyhedra are arranged into columns similar to those in Yb<sub>6</sub>Cr<sub>4+x</sub>Al<sub>43-x</sub> at  $x = 0, y = 0$ ; however, the columns are connected via interpenetrated V-centred [Al<sub>8</sub>V<sub>2</sub>] polyhedra (Fig. 3). The similarity of the stacking in these two compounds is reflected in their cell dimensions, which do not differ much along the hexagonal axes (V<sub>4</sub>Al<sub>23</sub>:  $c = 17.04 \text{ \AA}$ ).

## Experimental

The sample was prepared by arc melting and annealing at 773 K for three weeks.

### Crystal data

Yb<sub>6</sub>Cr<sub>5.76</sub>Al<sub>41.24</sub>  
 $M_r = 2450.45$   
 Hexagonal  
*P6<sub>3</sub>/mcm*  
 $a = 10.867 (1) \text{ \AA}$   
 $c = 17.554 (2) \text{ \AA}$   
 $V = 1795.3 (3) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 4.532 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 28 reflections  
 $\theta = 7.5\text{--}17^\circ$   
 $\mu = 18.148 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Needle  
 $0.064 \times 0.040 \times 0.032 \text{ mm}$   
 Silver

### Data collection

Philips PW1100 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction: analytical (*LSABS*; Blanc, Schwarzenbach & Flack, 1991)  
 $T_{\min} = 0.350, T_{\max} = 0.551$   
 3620 measured reflections  
 980 independent reflections

760 observed reflections  
 $[|F| > 3\sigma(|F|)]$   
 $R_{\text{int}} = 0.085$   
 $\theta_{\max} = 29.84^\circ$   
 $h = 0 \rightarrow 13$   
 $k = 0 \rightarrow 13$   
 $l = 0 \rightarrow 24$   
 2 standard reflections  
 frequency: 60 min  
 intensity variations: 1.5, 1.6%

### Refinement

Refinement on  $F$   
 $R = 0.053$   
 $wR = 0.036$   
 $S = 1.91$   
 760 reflections  
 53 parameters  
 $w = 1/\sigma^2(|F|)$   
 $(\Delta/\sigma)_{\max} = 0.0001$   
 $\Delta\rho_{\max} = 7.1 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -5.0 \text{ e \AA}^{-3}$

Extinction correction: Zachariasen (1968)  
 Extinction coefficient:  $g = 0.06 (2)$   
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

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

		x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Yb	12 (k)	0.46630 (6)	0	0.09586 (4)	0.0085 (2)
Cr(1)	6 (g)	0.2624 (4)	0	1/4	0.006 (1)
Cr(2)	2 (b)	0	0	0	0.007 (2)

Al(1)	24 (l)	0.2341 (4)	0.3952 (4)	0.1635 (2)	0.009 (1)
Al(2)	12 (k)	0.1560 (5)	0	0.1149 (3)	0.011 (2)
Al(3)	12 (k)	0.2529 (5)	0	0.5289 (3)	0.009 (2)
Al(4)	12 (j)	0.1481 (6)	0.5472 (6)	1/4	0.010 (2)
Al(5)	12 (i)	0.2495 (3)	2x	0	0.029 (2)
Al(6)†	8 (h)	1/3	2/3	0.1313 (2)	0.010 (1)
Al(7)	6 (g)	0.8498 (7)	0	1/4	0.006 (2)

† Al(6) site occupied by 44 (2)% Cr; set isotropic.

Table 2. *Interatomic distances* (<4 Å)

Yb—Al(4)	×2	3.044 (6)	Al(2)—Al(7)	×2	2.897 (6)
Yb—Al(5)	×2	3.057 (5)	Al(2)—Al(2)	×2	2.936 (7)
Yb—Al(1)	×2	3.062 (4)	Al(2)—Yb		3.389 (4)
Yb—Al(3)		3.190 (4)	Al(2)—Al(5)	×2	3.900 (8)
Yb—Al(6)	×2	3.219 (1)	Al(3)—Al(2)		2.737 (6)
Yb—Al(1)	×2	3.232 (8)	Al(3)—Al(5)	×2	2.740 (9)
Yb—Al(3)		3.270 (4)	Al(3)—Cr(2)		2.795 (8)
Yb—Al(5)	×2	3.369 (5)	Al(3)—Al(2)	×2	2.837 (11)
Yb—Al(2)		3.389 (4)	Al(3)—Al(1)	×2	2.885 (6)
Yb—Yb		3.444 (1)	Al(3)—Al(3)	×2	2.930 (12)
Yb—Cr(1)		3.498 (2)	Al(3)—Yb		3.190 (4)
Cr(1)—Al(7)	×2	2.478 (4)	Al(3)—Yb		3.270 (4)
Cr(1)—Al(2)	×2	2.638 (5)	Al(4)—Cr(1)		2.681 (6)
Cr(1)—Al(1)	×4	2.681 (8)	Al(4)—Al(1)	×2	2.730 (14)
Cr(1)—Al(4)	×2	2.681 (6)	Al(4)—Al(6)	×2	2.732 (12)
Cr(1)—Yb	×2	3.498 (2)	Al(4)—Al(1)	×2	2.764 (6)
Cr(2)—Al(2)	×6	2.635 (6)	Al(4)—Al(4)		2.787 (17)
Cr(2)—Al(3)	×6	2.795 (8)	Al(4)—Yb	×2	3.044 (6)
Al(1)—Al(6)		2.647 (8)	Al(4)—Al(4)	×2	3.062 (24)
Al(1)—Cr(1)		2.681 (8)	Al(5)—Al(5)	×2	2.734 (13)
Al(1)—Al(2)		2.709 (8)	Al(5)—Al(3)	×2	2.740 (9)
Al(1)—Al(4)		2.730 (14)	Al(5)—Al(6)	×2	2.794 (6)
Al(1)—Al(4)		2.764 (6)	Al(5)—Yb	×2	3.057 (5)
Al(1)—Al(7)		2.792 (9)	Al(5)—Al(1)	×2	3.057 (4)
Al(1)—Al(3)		2.885 (6)	Al(5)—Yb	×2	3.369 (5)
Al(1)—Al(1)		3.032 (7)	Al(5)—Al(2)	×2	3.900 (8)
Al(1)—Al(1)		3.038 (4)	Al(6)—Al(1)	×3	2.647 (8)
Al(1)—Al(5)		3.057 (4)	Al(6)—Al(4)	×3	2.732 (12)
Al(1)—Yb		3.062 (4)	Al(6)—Al(5)	×3	2.794 (6)
Al(1)—Yb		3.232 (8)	Al(6)—Yb	×3	3.219 (1)
Al(2)—Cr(2)		2.635 (6)	Al(7)—Cr(1)	×2	2.478 (4)
Al(2)—Cr(1)		2.638 (5)	Al(7)—Al(1)	×4	2.792 (9)
Al(2)—Al(1)	×2	2.709 (8)	Al(7)—Al(7)	×2	2.827 (9)
Al(2)—Al(3)		2.737 (6)	Al(7)—Al(2)	×4	2.897 (6)
Al(2)—Al(3)	×2	2.837 (11)			

The structure was solved by *MULTAN87* (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and refined by least-squares techniques varying the scale factor, isotropic extinction, atomic positional and anisotropic displacement parameters. The Al(6) site, about half occupied by Cr, was set isotropic and its occupancy parameter was refined. *Xtal3.2* (Hall, Flack & Stewart, 1992) was used for the data reduction and structure refinement. The high value of the displacement parameter of the Al(5) site has been noted. Refinement of the occupancy and displacement parameters of the Al(5) site did not improve the results.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Rietveld Refinement of the Structures of Dry-Synthesized $M\text{Fe}^{\text{III}}\text{Si}_2\text{O}_6$ Leucites ( $M = \text{K}, \text{Rb}, \text{Cs}$ ) by Synchrotron X-ray Powder Diffraction

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## Abstract

Analyses of high-resolution synchrotron X-ray powder diffraction patterns of dry-synthesized  $M\text{Fe}^{\text{III}}\text{Si}_2\text{O}_6$  leucites ( $M = \text{K}, \text{Rb}, \text{Cs}$ ) showed that the K- and Rb-containing leucites (iron potassium silicate,  $\text{KFeSi}_2\text{O}_6$ , and iron rubidium silicate,  $\text{RbFeSi}_2\text{O}_6$ ) each have a tetragonal  $I4_1/a$  structure and the Cs-containing leucite (caesium iron silicate,  $\text{CsFeSi}_2\text{O}_6$ ) has a cubic  $Ia\bar{3}d$  structure. The structures of these materials have been refined by the Rietveld method. In  $\text{CsFeSi}_2\text{O}_6$  leucite,  $\text{Fe}^{\text{III}}$  and Si are disordered on tetrahedral framework sites as required by space-group constraints. In  $\text{KFeSi}_2\text{O}_6$  leucite, Fe shows significant ordering and is concentrated on the  $T_3$  tetrahedral site.  $\text{RbFeSi}_2\text{O}_6$  leucite shows less pronounced  $T$ -site ordering reflecting the fact that it is closer to the tetragonal–cubic phase transition at which the  $T$  sites become identical.