JOURNAL OF SOLID STATE CHEMISTRY 49, 263–268 (1983)

# A Relation between the Structures of $Ce_{24}Co_{11}$, $Ru_7B_3$, and Pyrochlore

HARRY NYMAN

*Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, Australian Capital Territory 2600, Australia*

Received October 21, 1982; in revised form March 28, 1983

The structure of $Ce_{24}Co_{11}$ can be described as twinned pyrochlore. The twinning operation creates layers with the $Ru_7B_3$-type structure in the twin planes.

## Pyrochlores

Hexagonal tungsten bronze (HTB), which is a well-known structure type, can be described in terms of nets (*1*). In that context an HTB layer is a 3.4.6.4. net of corner-connected octahedra.[1] In the structure of HTB itself these nets are stacked on top of each other which gives a structure with parallel hexagonal tunnels running perpendicular to the layers. The HTB layer is a common building element in crystal structures. Usually, maybe always, the octahedra are tilted around axes in the plane of the layer. The octahedral framework of pyrochlore can be thought of as a cubic arrangement of HTB layers, i.e., four intersecting layers arranged with tetrahedral symmetry, which means a stacking of HTB layers along each body-diagonal of a cube. In this structure the hexagonal tunnels are intersecting and running in the [110], [011], and [101] directions. In a consideration of different kinds of pyrochlores, we described the structure of $Cr_4Al_{13}Si_4$ ($F\bar{4}3m$, $a$ = 10.917 Å) as the octahedral framework of pyrochlore (with empty octahedra) (*2*). Twelve of the thirteen Al atoms in the formula make up the framework. The tunnels are occupied by alternating large $AlSi_4$ tetrahedra and small $Cr_4$ tetrahedra. The tetrahedra can be made a second framework interpenetrating the octahedral framework by letting the $Cr_4$ tetrahedra become $Cr_4Si_4$ stellae quandrangulae (SQs). A *stella quandrangula* is a tetrahedron with a cap on every face (*2*). A projection of the structure of $Cr_4Al_{13}Si_4$ is shown in Fig. 1.

It is possible to insert trigonal prisms between the $AlSi_4$ tetrahedra and the central octahedron of every second pyrochlore unit. (A pyrochlore unit is an octahedron sharing four of its faces (tetrahedrally) with other octahedra.) The prisms share triangular faces with both the tetrahedra and the octahedra. In the lower left part of Fig. 1 are shown four prisms around one octahedron. Due to the size of the $AlSi_4$ tetrahedra, the prisms become slightly tapered in this particular compound. That means that

[1] Strictly, it is not possible to have a net of polyhedra. However, if we only consider the corners of the octahedra common to more than one octahedron, they describe a 3.4.6.4 net.



0022-4596/83 $3.00

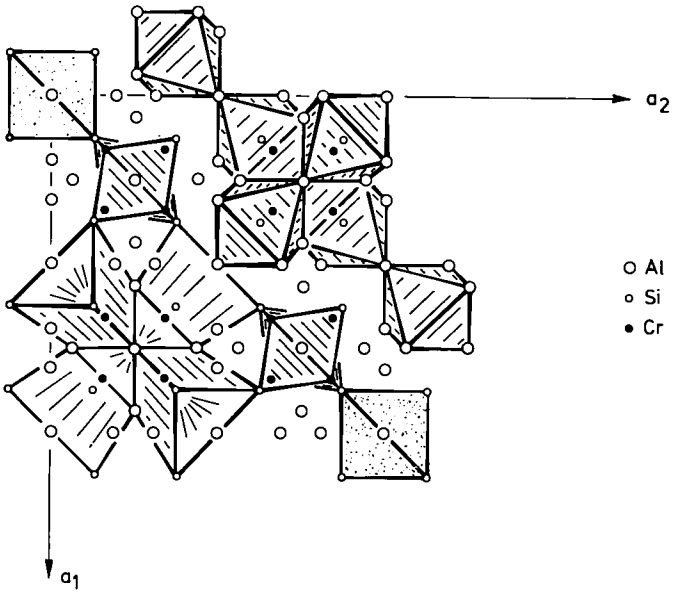


FIG. 1. The structure of $Cr_4Al_{13}Si_4$ projected along [001]. In the upper right the octahedral pyrochlore framework is fitted to the Al atom array. Parts of the interpenetrating $AlSi_4$–$Cr_4Si_4$ "stuffing" are shown in the upper left and lower right. The possibility of using $Al_3Si_3$ trigonal prisms in the description of the structure is indicated in the lower left.

the "stuffed" pyrochlore, $Cr_4Al_{13}Si_4$, can be described in two different ways: either as a framework of $Al_6$ octahedra interpenetrated by another framework of corner-connected $Cr_4Si_4$ SQs and $AlSI_4$ tetrahedra or as an edge- and corner-connected framework of $Al_3Si_3$ trigonal prism with isolated $Al_6$ octahedra and $Cr_4Si_4$ SQs in its cavities. (The isolated octahedra arise from the fact that only every second of the pyrochlore units participates in forming the prisms.)

Figure 2 shows two different projections of an idealized "stuffed pyrochlore" structure in hexagonal setting (the SQs are left out for clarity). In the left part of the figure an octahedral framework with isolated tetrahedra in its cavities (only one tetrahedron is shown in hatched lines) is fitted to the atomic array. This corresponds to the $Al_6$ octahedra and $AlSi_4$ tetrahedra of $Cr_4Al_{13}Si_4$ mentioned above. The same atomic array can also be described as a framework of trigonal prisms with isolated octahedra (only one shown) in its cavities as shown in the right part of Fig. 2, corresponding to the $Al_3Si_3$ prisms and the $Al_6$ octahedra of $Cr_4Al_{13}Si_4$.

The framework of prisms is actually 3.4.6.4 nets of connected prisms oriented in the same way as the HTB layers in pyrochlore mentioned above. We call these nets of prisms $Ru_7B_3$ layers, because the structure of $Ru_7B_3$ (*3*) is a simple stacking of these layers on top of each other (Fig. 3). Of course, in this case the prisms are centered by B atoms.

The left part of Fig. 2 also shows that the pyrochlore structure can be thought of as HTB layers separated by layers of isolated octahedra.

Several cases where this octahedral framework is collapsed are known. One way to collapse the framework is to take away a layer of isolated octahedra and (by a rotation of 60°) let the two opposing HTB layers share corners as in HTB itself. The

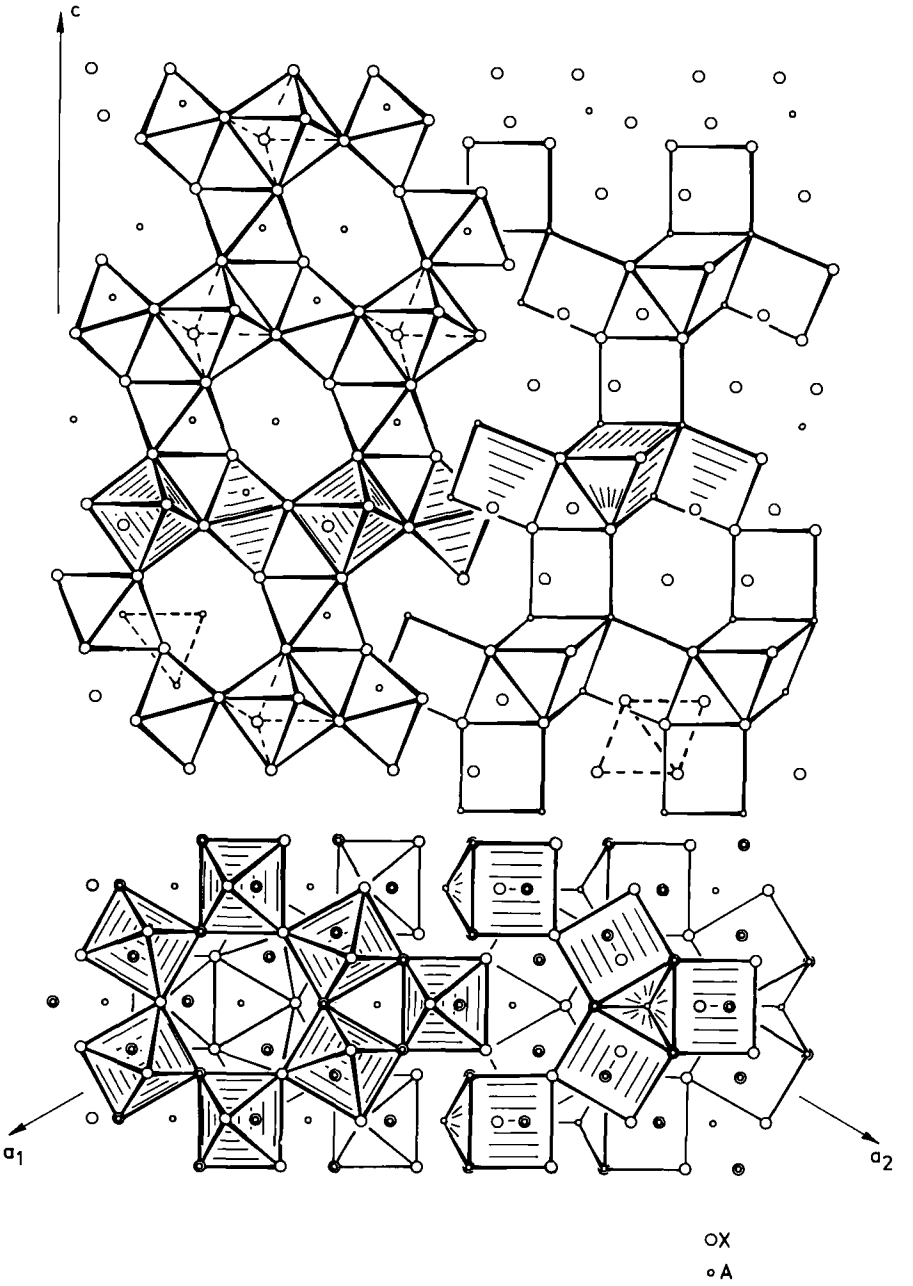


FIG. 2. Two projections [on $(11\bar{2}0)$ and (0001)] of an ideal pyrochlore framework drawn with hexagonal unit cell. X-Circles represent position *48 (f)* (*Fd3m*) of the pyrochlore structure, which creates the octahedral framework. A-Circles represent the "stuffing" of the cavities with tetrahedra. The right half of the figure shows the alternative description of the structure; edge- and corner-connected $A_3X_3$ trigonal prisms with isolated $X_6$ octahedra in the cavities. The shaded part is one HTB layer *left* and one $Ru_7B_3$-layer *right*.

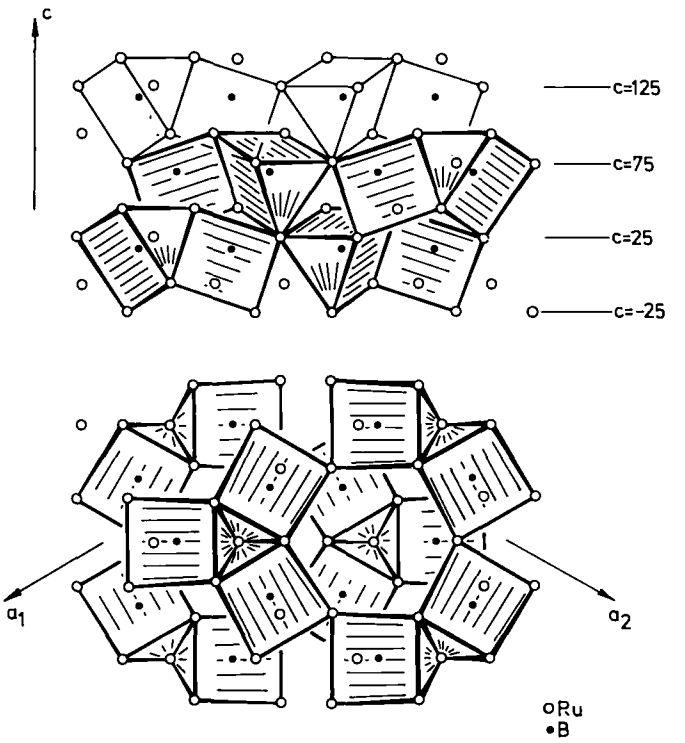


FIG. 3. The structure of $Ru_7B_3$ projected on $(11\bar{2}0)$ and (0001).

HTB layers can also collapse further to share edges, thereby necessarily distorting the edge-sharing octahedra. Examples of these types of collapses are found in several types of oxides (*4–8*).

Another way to collapse the pyrochlore framework is to remove an HTB layer, rotate one of the two remaining parts 60° around the three-fold axis, and let the two opposing "isolated-octahedra" layers share faces. That is the way pyrohlore is collapsed in the structure of $Ce_{24}Co_{11}$.

## *$Ce_{24}Co_{11}$*

The X-ray structure determination of $Ce_{24}Co_{11}$ was done by Larson and Cromer in 1962 (*9*). The structure is hexagonal, *P6mc*, with $a = 9.587$ Å and $c = 21.825$ Å, and is shown in Fig. 4. The figure shows that in this structure too, it is possible to use two different frameworks to describe the atomic array; either a framework of empty $Ce_6$ octahedra (left part of Fig. 4) or a framework of $CoCe_6$ prisms (right part of Fig. 4).

When we collapse the pyrochlore framework, in the way described above, by pulling out every second HTB layer, the effect on the trigonal-prism framework (the right part of Fig. 2) is that of taking away every second of the isolated, upright-prism layers. After rotating the remaining pieces and connecting them together we end up with the framework shown in the right part of Fig. 4.

If we look at the octahedral framework of $Ce_{24}Co_{11}$ (Fig. 4, left) it is obvious that it is twinned pyrochlore. Slabs of pyrochlore are sharing faces with each other in mirror planes. The right part of Fig. 4 shows that it is also possible to describe the structure as an intergrowth of the $Cr_4Al_{13}Si_4$ structure,

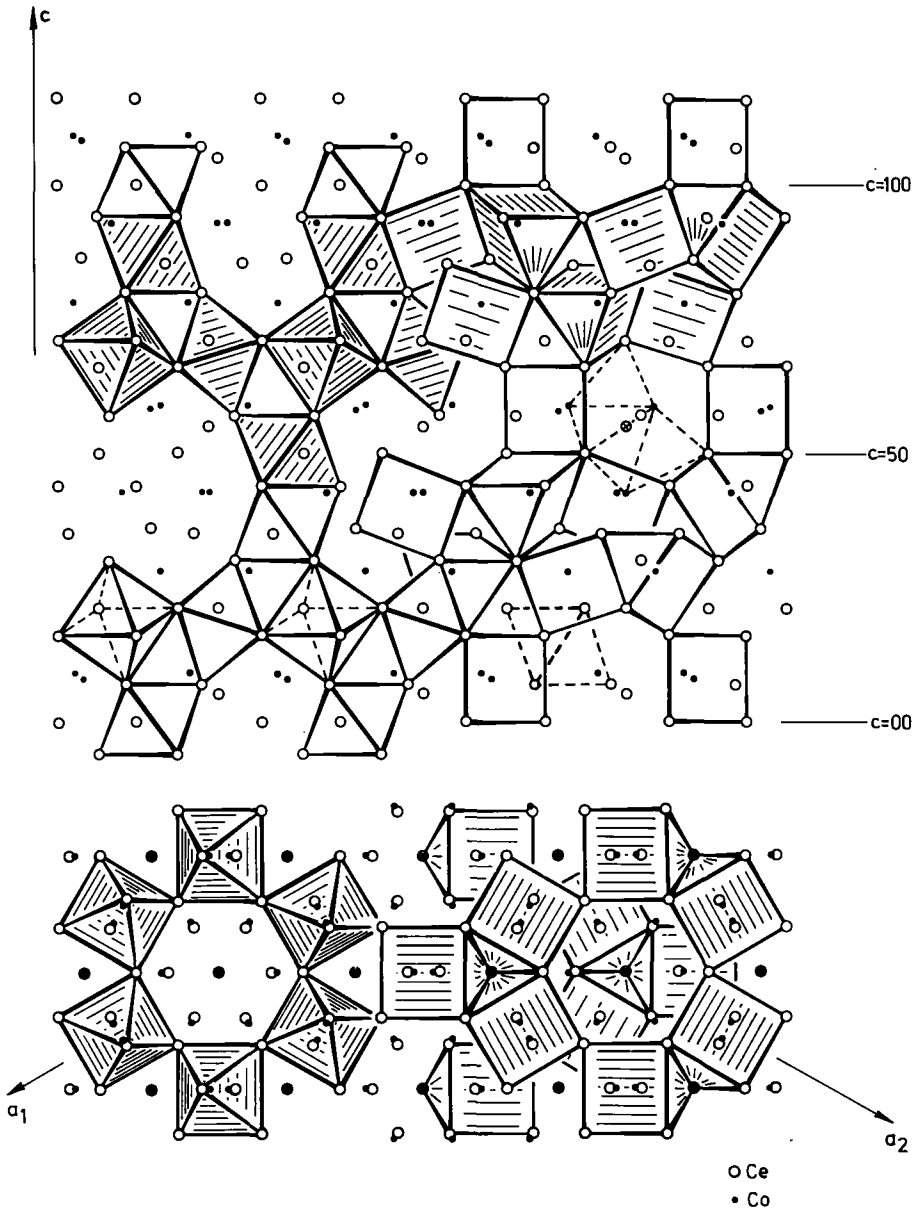


FIG. 4. Two projections [on $(11\bar{2}0)$ and (0001)] of the structure of $Ce_{24}Co_{11}$. The left and right halves of the figure show two alternative ways to describe the structure (as in Fig. 2). The shaded parts in the $(11\bar{2}0)$ projection are a lamella of pyrochlore, *left*, and a lamella of $Ru_7B_3$, *right*.

with $Ru_7B_3$ double layers created in the twin planes. The cavities in the prism framework are occupied in the same way as in the structure of $Cr_4Al_{13}Si_4$, i.e., with SQs and $Ce_6$ octahedra. The SQs in $Ce_{24}Co_{11}$ are centered by a Ce atom so they become $Co_4Ce_5$ SQs. One such $Co_4Ce_5$ SQ (with its central atom indicated by a crossed circle)

and one $Ce_6$ octahedron are shown in hatched lines in the right part of Fig. 4. To summarize: in the structure of $Cr_4Al_{13}Si_4$ (= "stuffed" pyrochlore) the framework is uncollapsed, the prisms are empty, and the tetrahedron, face-sharing with the prisms, is occupied. In the structure of $Ce_{24}Co_{11}$ the same framework is collapsed, the prisms are occupied, the tetrahedron is empty but the center of each SQ is occupied.

*Pu–Ce–Co*

In the ternary system Pu–Ce–Co some interesting phases have been found (*10*). One phase $(Pu,Ce)_7Co_3$ was reported to be hexagonal ($a$ = 9.358 Å, $c$ = 5.986 Å) and isostructural with $Th_7Fe_3$ which has the $Ru_7B_3$-type structure. Another phase, with the same total composition $(Pu,Ce)_7Co_3$ was said to be face-centered cubic with $a$ = 13.49 Å and containing 10 formula units per unit cell.

A projection of a face-centered cubic cell, with $a$ = 13.49 Å, along a three-fold axis gives a hexagonal cell with $a_{hex} = a$ cube/$\sqrt{2}$ = 13.49/$\sqrt{2}$ = 9.539 Å. That value is to be compared with the $a$ axes of $Ce_{24}Co_{11}$ and the hexagonal $(Pu,Ce)_7Co_3$ which are 9.587 and 9.358 Å, respectively. The similarity in the $a_{hex}$ values *could* mean that the structure of the cubic form of $(Pu,Ce)_7Co_3$ is built of the same $Ru_7B_3$ layers as the two other structures are. If that is the case, a probable structure for the cubic $(Pu,Ce)_7Co_3$ could be modeled. We start with a trigonal-prism framework as in "stuffed" pyrochlore (Fig. 2). The unit cell is going to contain 16 prisms (a hypothetical structure of that kind was mentioned in our paper about pyrochlores (*2*)). The stoichiometry of the framework is $(Pu,Ce)_{40}Co_{16}$, with the prisms centered by Co atoms. By filling the cavities of the prism framework in the same way as in the structure of $Ce_{24}Co_{11}$, i.e., with isolated $(Pu,Ce)Co_4$ tetrahedra (or $(Pu,Ce)_5Co_4$ SQs if we connect them to the prism framework) plus isolated $(Pu,Ce)_6$ octahedra, we get a total stoichiometry of $(Pu,Ce)_{40}Co_{16} + 4(Pu,Ce)_7Co_4 + 4(Pu,Ce)Co_6 = (Pu,Ce)_{68}Co_{32}$. This is to be compared with 10 formula units of $(Pu,Ce)_7Co_3$ per unit cell mentioned by Ellinger *et al.* (*10*). So, the cubic $(Pu,Ce)_7Co_3$ *could* have a "stuffed" pyrochlore structure, the hexagonal $(Pu,Ce)_7Co_3$ has a *completely* collapsed "stuffed" pyrochlore structure, and the structure of $Ce_{24}Co_{11}$ is a *partly* collapsed "stuffed" pyrochlore.

Finally, it is very hard to resist quoting from the paper by Larson and Cromer (*9*): ". . . for there is no place in the present structure [$Ce_{24}Co_{11}$] where a structural unit such as that of $Ce_7Ni_3$ exists." $Ce_7Ni_3$ is isostructural with $Ru_7B_3$.

## References


1. M. O'Keeffe and B. G. Hyde, *Phil. Trans. Roy. Soc. London Ser. A* **295,** 553–623 (1980).
2. H. Nyman, S. Andersson, B. G. Hyde, and M. O'Keeffe, *J. Solid State Chem.* **26,** 123–131 (1978).
3. B. Aronsson, *Acta Chem. Scand.* **13,** 109–114 (1959).
4. M. Gasperin, *Acta Crystallogr. Sect. B* **33,** 398–402 (1976).
5. G. D. Fallon and B. M. Gatehouse, *J. Solid State Chem.* **22,** 405–409 (1977).
6. C. Michel, A. Guyomarc'h, and B. Raveau, *J. Solid State Chem.* **22,** 393–403 (1977).
7. G. Desgardin, C. Robert, D. Groult, and B. Raveau, *J. Solid State Chem.* **22,** 101–111 (1977).
8. K. Yagi and R. S. Roth, *Acta Crystallogr. Sect. A* **34,** 765–781 (1978).
9. A. C. Larson and D. T. Cromer, *Acta Crystallogr.* **15,** 1224–1227 (1962).
10. F. G. Ellinger, C. C. Land, K. A. Johnson, and V. O. Struebing, *Trans. Amer. Inst. Min. Eng.* **236,** 1577–1588 (1966).