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A Structural Relationship between Sr_6Mg_{23} and $SrMg_4$

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The crystal structures of Sr_6Mg_{23} and $SrMg_4$ are described by using "γ-brass clusters." This description gives a rather simple relationship between the two structures.

In an earlier paper (*1*) we showed how to obtained the "γ-brass cluster" (*2*) by capping all the edges of a *stella quadrangula* (*SQ*). The final product of the capping is a distorted cube-octahedron surrounding 14 atoms. In the same paper we also described the Mn atom arrangement in the structure of the Th_6Mn_{23} as an array of connected *partly* capped SQs. However, the Th atoms can also be thought of as caps of the SQ and thereby completing the "γ-brass cluster." The different sizes of Mn and Th atoms distort the ideal "γ-brass cluster" in a way to make the outer shell, the distorted cube-octahedron, slightly bigger than ideal (*3*).

The structure of Sr_6Mg_{23} (*4*) is isostructural with Th_6Mn_{23}. A projection of the cubic structure (a = 14.914 Å, $Fm3m$) along the [001] direction is shown in Fig. 1. In the upper left part of Fig. 1 one partly capped SQ is shown connected to a fully capped SQ (right). If only the Th atoms are considered, the polyhedron in the lower left part of Fig. 1 is the building unit. The unit is, as mentioned above, a distorted cube-octahedron (the atomic parameter for Sr is x = 0.2041; x = 0.25 should make the cube-octahedron regular).

In their description of the structure of Sr_6Mg_{23}, Wang *et al.* (*4*) use the motif of an octahedron of Sr atoms surrounded by 50 Mg atoms. Another way to look at the structure is indicated in the lower right part of Fig. 1. The Th atoms described a corner-connected array of two different sized octahedra, which means a distorted perovskite. Elpasolite, NaK_2AlF_6 (*5*), with x_F = 0.219 is a perovskite distorted in the same way as Sr_6Mg_{23} with Na atoms centering the big octahedra and Al atoms centering the small

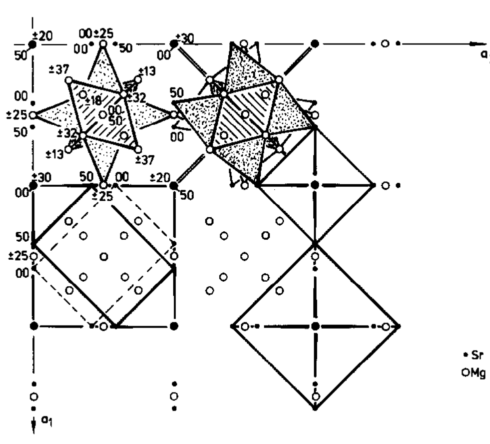

FIG. 1. The structure of Sr_6Mg_{23} projected on (001).

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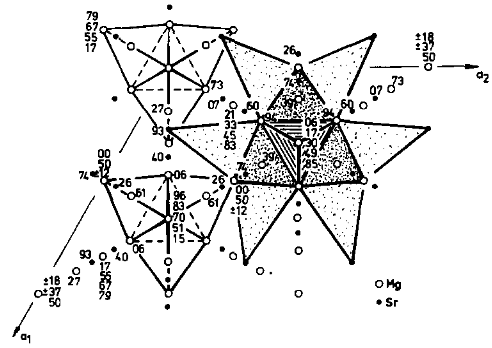

FIG. 2. The structure of Sr_6Mg_{23} projected on (111).

ones. That means that the structure of Sr_6Mg_{23} is an elpasolite with the small octahedron empty, an Mg atom centering the big octahedron and 14 Mg atoms in every cube-octahedron. Because the latter share all rectangular faces and have a Mg atom in every such face, the content of the cube-octahedron is reduced to 11 Mg atoms, which gives the stoichiometry:

$$NaK_2AlF_6 \doteqdot Mg(Mg_{11})_2\square Sr_6 = Sr_6Mg_{23}.$$

Figure 2 shows the structure of Sr_6Mg_{23} projected along the [111] direction which gives a hexagonal cell with

$$a_{hex} = \frac{a_{cube}}{2^{1/2}} = 10.546\ \text{Å} \qquad \text{and}$$

$$c_{hex}{}' = 3^{1/2} \cdot a_{cube} = 25.832\text{Å}.$$

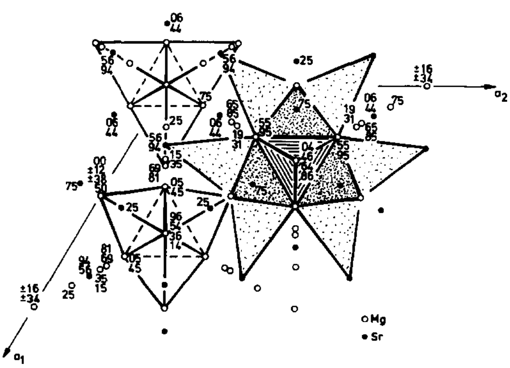

FIG. 3. The structure of $SrMg_4$ projected along the c axis.

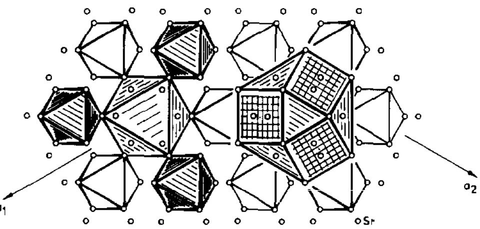

FIG. 4. The corner-connected array of Sr atom octahedra in Sr_6Mg_{23}. To the right, one cube octahedron is indicated.

Three SQs at different levels are pictured, one with some caps and two without caps. The projection of the structure of Sr_6Mg_{23} along the [111] direction clearly shows the similarity between Sr_6Mg_{23} and $SrMg_4$ shown in Fig. 3. The structure of $SrMg_4$ (*4*) is hexagonal (a = 10.511 Å, c = 28.362 Å, $P6_3/mmc$) and has the same building unit the fully capped SQ, as Sr_6Mg_{23}. However, the arrangement of the units is different.

To simplify the pictures of the two structures we only look at the octahedral array of Sr atoms, Figs. 4, 5. As can be seen from Fig. 5, the octahedra in Sr_6Mg_{23} are all corner-connected, but in $SrMg_4$ there is both corner-connection and face-sharing between the octahedra. The relation between Sr_6Mg_{23} and $SrMg_4$ is the same as the relation between cubic $BaTiO_3$, which has the perovskite structure, and hexagonal Ba TiO_3 (*6*). In the titanates the octahedra are of only one size and the transformation from the cubic form to the hexagonal one is

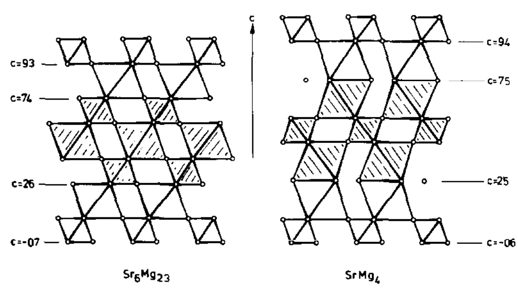

FIG. 5. A projection on (0010) of the octahedral arrangement in (a) Sr_6Mg_{23} and (b) $SrMg_4$.

only a change of stacking sequence of close packed layers, from c to hcc (*7*). The operation is actually to insert two twin planes perpendicular to the body diagonal of the cubic $BaTiO_3$. If the shaded part of the structure in Fig. 5a is removed and a mirror plane is placed at each cut, the structure pictured in Fig. 5b is obtained. That is; the structure of $SrMg_4$ is twinned Sr_6Mg_{23} with twin planes at $c = 25$ and $c = 75$ (hundredths of the c axis). Of course the Mg atoms are also affected by this twin operation. Fig. 6a shows the columns of face-sharing octahedra and cube-octahedra in Sr_6Mg_{23}. Identical columns occur around 0, 0, z; $\frac{2}{3}$, $\frac{1}{3}$, z; and $\frac{1}{3}$, $\frac{2}{3}$, z, although at different levels. The twin operation changes the columns to the shapes shown in Fig. 6b, i.e., alternating pairs of octahedra and pairs of cube-octahedra, around $\frac{2}{3}$, $\frac{1}{3}$, z and $\frac{1}{3}$, $\frac{2}{3}$, z, and the right column of Fig. 6b around 0, 0, z. In both cases the columns share rectangular faces with each other.

The analogy in the case of $BaTiO_3$ is that in the hexagonal (twinned) form of $BaTiO_3$ one third of the cube-octahedra, all lying along 0, 0, z, are "twinned." (A "twinned cube octahedron" is the polyhedron of nearest neighbors in hcp). Twinning of the *irregular* cube octahedron in Sr_6Mg_{23} gives the elongated "twinned cube octahedron," shown in the right part of Fig. 6b, which, due to the twinning, contains three additional Mg atoms, that is, "14" Mg-atoms instead of "11." In $SrMg_4$ both sizes of octahedra are empty. Therefore, the stoichiometry is:

$$BaTiO_3 = Ba_3Ti_3O_9 \div (Mg_{11})_2Mg_{14}\square Sr_9 = SrMg_4.$$

By using fully capped *stellae quadrangulae,* which is a very accurate description of

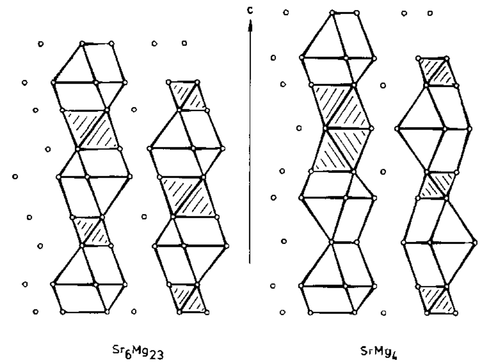

FIG. 6. A projection on (0010) of the different kinds of columns in (a) Sr_6Mg_{23} and (b) $SrMg_4$.

the "γ-brass cluster" (*1*), it is possible to show that $SrMg_4$ is twinned Sr_6Mg_{23}. In contrast to γ-brass, Cu_5Zn_8, where the clusters are separate, and $Cr_4Si_4Al_{13}$, where they share corners (*3*), the connections between the clusters in Sr_6Mg_{23} and $SrMg_4$ are through common faces.

Note added in proof. Recently, the structure of Th_6Mn_{23} was described using the concept of "nested polyhedra." That description also uses cube-octahedra as building-elements. [B. CHABOT, K. CENZUAL, AND E. PARTHÈ, *Acta Crystallogr.* **A37**, 6–11 (1981).]

References

1. H. NYMAN AND S. ANDERSSON, *Acta Crystallogr. Sect. A* **35**, 580 (1979).
2. A. J. BRADLEY AND P. JONES, *J. Inst. Met.* **51**, 131 (1933).
3. H. NYMAN, Thesis, University of Lund, Lund Sweden (1979).
4. F. E. WANG, F. A. KANDA, C. F. MISKELL, AND J. K. ADEN, *Acta Crystallogr.* **18**, 24 (1965).
5. L. R. MORSS, *J. Inorg. Nucl. Chem.* **36**, 3876 (1974).
6. R. D. BURBANK AND H. T. EVANS, JR., *Acta Crystallogr.* **1**, 330 (1948).
7. A. F. WELLS, "Structural Inorganic Chemistry," 4th ed., p. 481. Oxford Univ. Press (Clarendon), Oxford, 1975.