JOURNAL OF SOLID STATE CHEMISTRY **41**, 23–26 (1982)

On the Relationship between the Structure of $CaFe_2O_4$ and Hollandite

C. M. PLUG

Gorlaeus Laboratories, Rijksuniversiteit, P. O. Box 9502, 2300 RA Leiden, The Netherlands

Received June 26, 1981

The relationship between the structure of $CaFe_2O_4$ and those of rutile and hollandite is shown. $CaFe_2O_4$ may be regarded as a glide reflection twin derivative of a distorted hollandite-type structure. On the basis of this structural relationship the possibility of the existence of compounds with intermediate structures is suggested.

Introduction

Rutile- (*1*), hollandite- (*2*), and $CaFe_2O_4$-(*3*) type structures have in common a MX_2 framework of octahedra. It has been pointed out by several authors (*4–7*) that rutile and hollandite are closely related. The hollandite framework is derived from rutile applying a regularly repeated rotation operation on columns of octahedra parallel to the rutile *c* axis.

In rutile, square tunnels occur as a result of the deformation from hexagonal close packing of the anions. This deformation produces a planar triangular coordination of the oxygen atoms connecting the octahedron strings. The double-octahedral strings in hollandite form two types of square tunnels. In the larger eightfold coordinated sites may accommodate cations of appropriate size. Filling all these sites a compound with composition AM_4X_8 is obtained.

Recently a number of ternary sulfides has been reported with composition AM_5S_8 (*8, 9*). These compounds crystallize with a stuffed and deformed hollandite-type structure. In this structure type the smaller hollandite tunnels are occupied by octahedrally coordinated cations and consequently also the larger tunnels cannot remain square. This is probably the reason why this structure is found only for sulfides and not for oxydes, the coordination of part of the anions being in favour of anion polarization.

In this paper we will describe this stuffed hollandite structure in more detail and show its relationship with the structure of $CaFe_2O_4$. The latter structure is found for many ternary sulfides. In view of the relationship derived the existence of intermediate structures is predicted.

Description of the Structures

Rutile

The structure of rutile may be idealized so that the oxygen atoms are in perfect hcp. This is easily seen in the projection along [001] (Fig. 1). Thus idealized, the rutile structure derives from the structure of

0022-4596/82/010023-04$02.00/0
Copyright © 1982 by Academic Press, Inc.
All rights of reproduction in any form reserved.

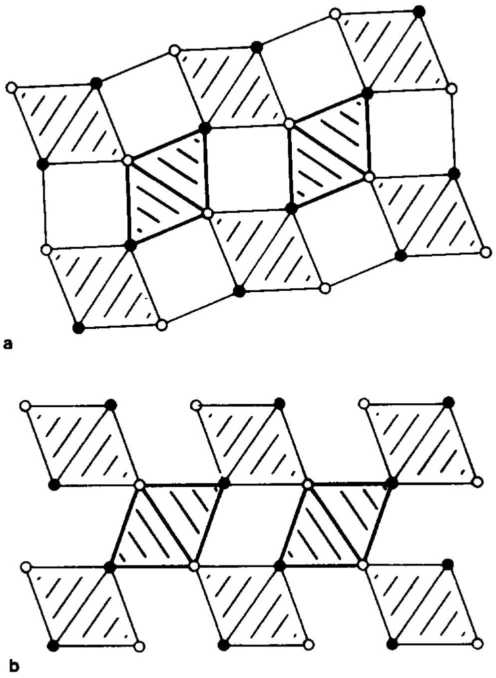

FIG. 1(a) Projection of the rutile structure along [001]. Open and filled circles represent oxygen atoms at $z = 0$ and $z = \frac{1}{2}$, respectively. (b) The rutile structure idealized to hcp.

NiAs by leaving half of the octahedral interstices empty. Allowing this substitution only in alternating layers a structure with composition M_3X_4 is obtained. This structure type is found, among others, in the compounds MMo_2S_4 (M = V, Cr, Fe, Co) (*10–12*). The cubic counterpart of this structure, that is an ordered vacancy superstructure of NaCl, is realized in $MnSn_2S_4$ (*13*).

Hollandite and Related Structures

Applying a regularly repeated rotation operation on the real rutile structure, the hollandite framework can be obtained. The same type of operation applied on rutile which has been idealized to hcp, yields a different, though closely related structure. The resulting framework is topologically equivalent to the hollandite framework, but both the larger and the smaller tunnels which are rectangular in hollandite are now diamond shaped with angles of 70.5°. (Fig. 2).

As in "hcp" rutile, the smaller tunnels consists of perfect octahedra which may be occupied by cations. In such a case a structure with composition M_5X_8 is obtained. Analogous to the hollandite structure, the larger tunnels can accommodate large cations. This situation is met, though not exactly, in the structures of TIV_5S_8 (*8*) and of MCr_5S_8 (M = K, Rb, Cs) (*9*).

The real structures differ slightly from the ideal structures derived from hcp. In the latter, part of the octahedra share faces with two other octahedra. In the real structure this is reduced to one by a simple shift in the octahedral framework, (Fig. 3) leaving the stoichiometry unaltered. The structures reported for TIV_5S_8 and MCr_5S_8 are monoclinic, SG C2 or *C2/m* and the observed values for the monoclinic angle β are very close to the calculated value for the ideal structure. For TIV_5S_8, e.g., β = 103.94°, to be compared to β = 103.26° from $\tan \beta = -3(2)^{1/2}$.

$CaFe_2O_4$

The orthorhombic structure of $CaFe_2O_4$

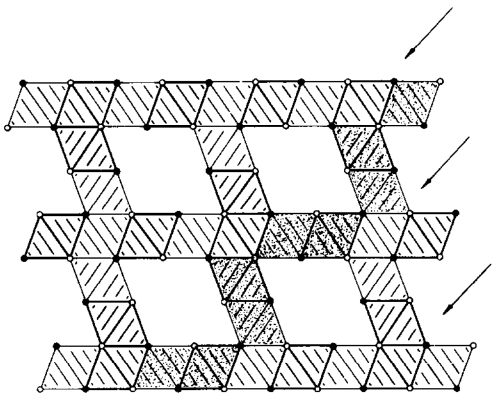

FIG. 2. Deformed hollandite framework derived from hcp rutile by a regularly repeated rotation operation.

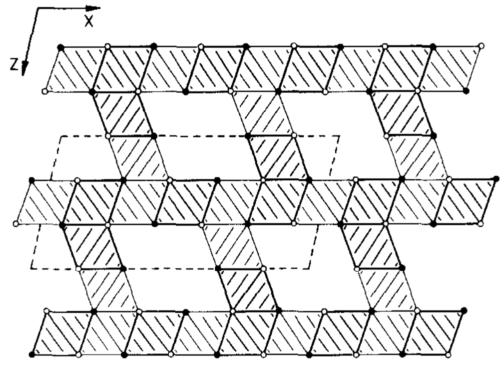

FIG. 3. The structure of TlV_5S_8 and MCr_5S_8 projected along the b axis.

has first been reported by Decker and Kasper in 1957 (*3*). In the last decades many other compounds have been found with the same structure. These include a large number of ternary sulfides. The structure consists of a network of FeO_6 octahedra with trigonal prismatic interstices accommodating the Ca atoms inbetween. All atoms are positioned on $z = \frac{1}{4}$ or $z = \frac{3}{4}$ in space group *Pnam*. From the projection of the structure along [001] (Fig. 4) it is seen that double octahedra chains are corner connected in a similar way as in the hollandite structure. This observation forms the basis of the structural relation of these structures derived further on.

Structural Relations

Both in Fig. 2 and Fig. 4 bands of octahedra are indicated by shading. These bands in both structures are very much alike, the only difference being the angle between two adjacent double chains. This angle α is 70.5° in the case of the ideal M_5X_8 framework, provided the structure is built with perfect octahedra. In the $CaFe_2O_4$ structure (Fig. 4), again with perfect octahedra, α is 53.13°, from $\tan \alpha = \frac{1}{2}$.

The structural relation between the hollandite structure and the $CaFe_2O_4$ structure is now readily seen. We start again with the hollandite framework of octahedra having a composition of M_4X_8, that is, leaving the small tunnels empty. Using the octahedron corners that connect the double chains as hinges, we may deform the structure until the diamond angle $\alpha = 53.13°$. Now a glide reflection operation is applied along the planes that bound the shaded octahedra band. These planes are indicated in Fig. 2 by arrows. The glide operation has to be in such a way that the centers of the larger and the smaller diamonds in the mirror plane coincide. Repeating this glide reflection operation regularly the structure of $CaFe_2O_4$ is obtained. The repeated glide mirror planes are of course symmetry operations of the $CaFe_2O_4$ structure and are positioned at $y = \frac{1}{4}$ and $y = \frac{3}{4}$ (cf. Fig. 4).

The deformation of the hollandite framework previous to the glide reflection operation is necessary in order to make the original and the glide-reflected part of the structure fit. The condition is that the length of the longer diagonal of the smaller diamond equals the length of the shorter diagonal of the large diamond. From this $\tan \alpha = \frac{1}{2}$ or $\alpha = 53.13°$. The fit condition is independent of the exact shape of the octa-

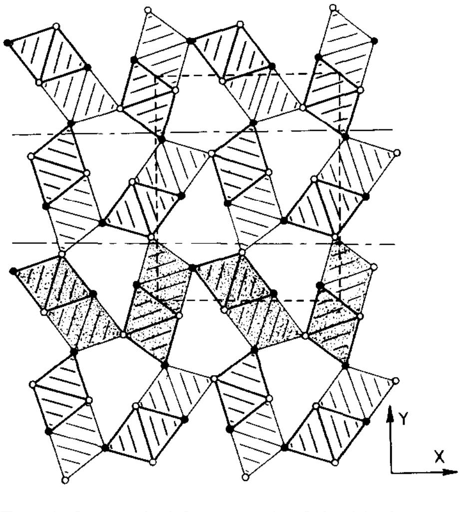

FIG. 4. Octahedral framework of the ideal structure of $CaFe_2O_4$ projected along [001].

hedra. It is interesting to note that in the real structure of $CaFe_2O_4$, in which the FeO_6 octahedra are slightly distored, $\alpha = 55.4^\circ$ (calculated from the experimental oxygen positions).

Discussion

The structure of $CaFe_2O_4$ may be described as a mimetic (that is regularly repeated) glide reflection twin of a distorted hollandite structure. Alternatively it can be regarded as a twin derivative of a mixed hexagonal-cubic close-packed array. Consequently it is another example of a structure derived by unit-cell twinning (*14*). The structure of $CaFe_2O_4$ may be compared to that of $CaTi_2O_4$ (*15*) (with which it is often confused), which has been described as unit-cell twinned ccp (*16*).

The structure of $CaTi_2O_4$ is a member of a vast family of structures, the members differing only in the frequency of twinning. The twinning operation additionally supplies a mechanism for introducing disorder when it is not repeated regularly. Experimental evidence which supports this description of twinned structures has been obtained in an electron microscope study on the system $MnS + Y_2S_3$ (*17*). Several structures, both with ordered and disordered twin planes have been observed.

It is suggestive that also in the case of twinned hollandite structures these phenomena may be observed. Intermediate phases and new structures are expected to be found in systems with compositions intermediate to hollandite (AM_4X_8) and AM_2X_4. Suitable and members of such a family are probably KCr_5S_8 (structure derived from hollandite) and $CaSc_2S_4$ or $SrSc_2S_4$ ($CaFe_2O_4$ structure).

References

1. R. W. G. Wyckoff: "Crystal Structures," Vol. 1, Interscience, New York (1968).
2. A. Byström and A. M. Byström, *Acta Crystallogr.* **3**, 146 (1950).
3. B. F. Decker and J. S. Kasper, *Acta Crystallogr.* **10**, 332 (1957).
4. A. D. Wadsley, *in* "Nonstoichiometric Compounds" (L. Mandelcorn, Ed.), p. 111. Academic Press, New York (1964).
5. L. A. Bursill and B. G. Hyde, *Nature (London) Phys. Sci.* **240**, 122 (1972).
6. B. G. Hyde, A. N. Bagshaw, M. O'Keeffe, and S. Andersson, *Annu. Rev. Mater. Sci.* **4**, 43 (1974).
7. L. A. Bursill, *Acta Crystallogr. Sect. B* **35**, 530 (1979).
8. L. Fournès, M. Vlasse, and M. Saux, *Mater. Res. Bull.* **12**, 1 (1977).
9. J. Huster, *Z. Anorg. Allg. Chem.* **447**, 89 (1978).
10. K. Anzenhofer and J. J. de Boer, *Acta Crystallogr. Sect. B* **25**, 1419 (1969).
11. R. Chevrel, M. Sergent, and J. Prigent, *C. R. Acad. Sci. Paris* **267**, 1135 (1968).
12. J. Guillevic, J. Y. Marouille, and D. Grandjean, *Acta Crystallogr. Sect. B* **30**, 111 (1974).
13. M. Wintenberger and J. C. Dumas, *Acta Crystallogr. Sect. B* **36**, 1993 (1980).
14. S. Andersson and B. G. Hyde, *J. Solid State Chem.* **9**, 92, (1974).
15. E. F. Bertaut and P. Blum, *Acta Crystallogr.* **9**, 121 (1956).
16. B. G. Hyde, S. Andersson, M. Bakker, C. M. Plug, and M. O'Keeffe, *Progr. Solid State Chem.* **12**, 273 (1979).
17. M. Bakker and B. G. Hyde, *Philos. Mag.* **38**, 615 (1978).