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NOTES

The Structures of $CaFe_2O_4(FeO)_n$ (n = 1, 2, 3) and Their Relationship to $CaTi_2O_4$

Recently Evrard *et al.* (*1*) synthesized the compounds $CaFe_2^{3+}Fe^{2+}O_5$, $CaFe_2^{3+}Fe_2^{2+}O_6$, and $CaFe_2^{3+}Fe_3^{2+}O_7$. They showed that these crystal structures are closely related to each other. Their description uses hypothetical structural blocks of composition $CaFe_2^{3+}O_4$ [with an atomic arrangement different from the known structure of $CaFe_2O_4$ (*2, 3*)] and varying numbers of blocks of composition FeO. This can be written as $CaFe_2O_4(FeO)_n$. Evrard *et al.* propose that the formally divalent Fe atoms are located in the FeO blocks of these structures.

Actually, the hypothetical $CaFe_2O_4$ arrangement occurring in the $CaFe_2O_4(FeO)_n$ compounds has been observed previously for a different chemical composition, namely, $CaTi_2O_4$ (*4*). The similarity between the $CaFe_2O_4$ and $CaTi_2O_4$ structures is that both are constructed of double rutile chains (*5*), that is, two fused rows of edge-sharing coordination octahedra around Fe^{3+} or Ti^{3+}, which share oxygen corners with neighboring double rutile chains. The difference between $CaFe_2O_4$ and $CaTi_2O_4$ lies in the nature of the condensation with neighboring chains. In $CaFe_2O_4$ this results in all oxygen atoms being shared between three different coordination octahedra (as also happens in rutile, TiO_2, or ramsdellite, MnO_2), while in $CaTi_2O_4$ one oxygen atom per formula unit is shared by two Ti octahedra, two are shared between three octahedra, and the fourth belongs to four different octahedra. As a consequence of this, parallel double octahedral chains in $CaTi_2O_4$ also share edges with each other, while in $CaFe_2O_4$ they do not. All these structures are characterized by one short cell constant of about 3.0 Å in a direction normal to the shared octahedral edge within the rutile-type chain. Thus they belong in one group with β-gallia, hollandite, psilomelane, and the gallium titanate type structures. These have recently been reviewed by Bursill (*6*). Schematic projections parallel to the short axis illustrating the relationship between the $CaTi_2O_4$ and $CaFe_2O_4(FeO)_n$ structures are presented in Fig. 1. The main remaining difference between the $CaTi_2O_4$ and $CaFe_2O_4(FeO)_n$ structures on one hand and all the other "3 Å" structures on the other hand is the joining of the multiple octahedral rutile chains. This is done by octahedral corners and edges in the former, and exclusively by corners in the latter. The chains joined sideways by common edges in the $CaFe_2O_4(FeO)_n$ structures correspond to layers of an NaCl-type arrangement (as in FeO). Thus these structures are intermediate between the only corner-sharing "3 Å" types and the NaCl type. They show that different joining mechanisms can be realized in the "3 Å" structures.

Table I lists the mean Fe–O bond lengths calculated from data in Ref. (*1*) for the various Fe sites in the $CaFe_2O_4(FeO)_n$ structures. When we compare these with the distances calculated on the basis of Shannon's (*7*) radii for Fe^{2+} and Fe^{3+} in high-spin octahedral environments (0.78 and 0.645 Å, respectively) and a radius of 1.39 Å for an oxygen atom in five-coordination we see that the overall mean calculated and observed Fe–O distances agree well. The Fe–O distances for individual Fe coordination octahedra do not indicate exclusive occu-

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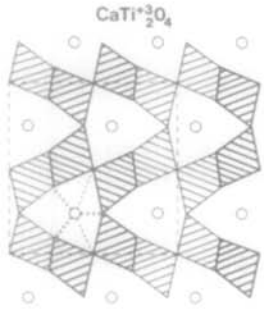
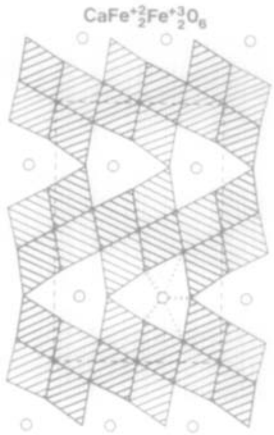




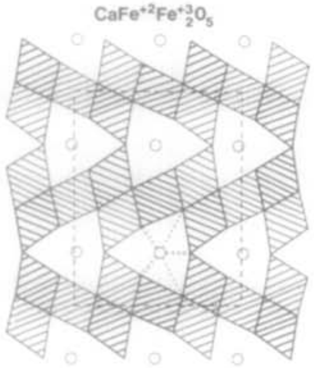
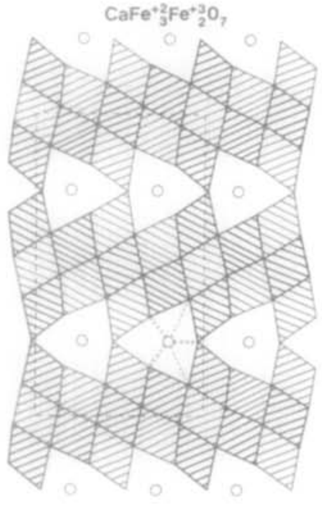


FIG. 1. Projections along the lengths of octahedral edge-sharing rutile-type chains in $CaTi_2O_4$ and $CaFe_2O_4(FeO)_n$. The shared octahedral edges correspond to the short diagonals of the rhombs indicating the view down the strings of octahedra. In the octahedra drawn by light lines the central cation is at a height of zero; in the boldly drawn octahedra it is at a height of 0.5. The Ca atoms, shown as circles, are alternately at heights zero and 0.5 as well. For one Ca atom in each figure the coordinating contacts are shown. The unit cells are outlined by dashed lines.



pations by either Fe^{2+} or Fe^{3+} ions. Instead all sites are statistically occupied. The Fe^{3+} occupancies listed in Table I were estimated from the bond lengths after adjustment for the overall Fe^{2+}-to-Fe^{3+} ratio. The proportions of octahedral Fe^{3+} occupation change from compound to compound. As we go from $CaFe_3O_5$ to $CaFe_5O_7$ the population of Fe^{3+} in the site Fe(3) in the $CaFe_2O_4$ block changes from 75% Fe^{3+} to 35% Fe^{3+}. In the sites labeled Fe(1) the proportions of the two valence states are approximately equal, while the Fe(2) site in $CaFe_5O_7$ is the one most populated by Fe^{2+} (80%). This is in keeping with observations on other "3 Å" oxide structures, where occupations of sites in the octahedral rutile

TABLE I

OBSERVED AND CALCULATED BOND LENGTHS (Å) AND Fe^{3+} OCCUPANCIES IN THE $CaFe_2O_4(FeO)_n$ STRUCTURES

	$CaFe_3O_5$	$CaFe_4O_6$	$CaFe_5O_7$
Calculated Fe–O bond lengths using Shannon's radii (*7*)			
Fe^{2+}–O	2.170	2.170	2.170
Fe^{3+}–O	2.035	2.035	2.035
Mean Fe–O	2.080(2/3)	2.103(2/4)	2.116(2/5)
Observed Fe–O bond lengths after Evrard *et al.* (*1*)			
Fe(1)–O	[4*a*] 2.109(0.50)	[8*f*] 2.099(0.55)	[8*f*] 2.098(0.55)
Fe(2)–O	—	—	[4*a*] 2.143(0.20)
Fe(3)–O	[8*f*] 2.078(0.75)	[8*f*] 2.118(0.45)	[8*f*] 2.123(0.35)
Mean Fe–O	2.088(2/3)	2.109(2/4)	2.117(2/5)

Note. The Fe^{3+} contents are expressed as $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ and given in parentheses following the bond length values. The equipoints occupied by the Fe atoms are in square brackets preceding the bond length values.

chains exclusively by divalent metal ions have not yet been observed.

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