

Fig. 6 Effect of molecular weight. Polyox, various grades, 30–36 mesh (0.46 mm), 0.86 p.p.m., 17° C. *a*, WSR N-10 (molecular weight 100,000); *b*, WSR 205 (molecular weight 600,000); *c*, WSR 301 (molecular weight 4,000,000); *d*, Coagulant 1 (molecular weight >5,000,000).

practical side, it suggests possible economies in the use of polymers, particularly PEO, in recirculating and non-recirculating systems; in the former the object should be to stabilise aggregates, in the latter to obtain the correct size aggregates at the right time.

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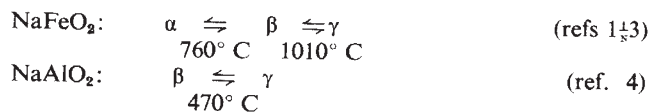
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NaAlO₂ and NaFeO₂ Polymorphism

THE polymorphism of NaAlO₂ and NaFeO₂ is well known. Both oxides form β and γ polymorphs, and although their crystal structures are known, the relationship between the β and γ polymorphs has not been described. This relationship is described here and from it a simple topotactic mechanism for the $\beta \rightleftharpoons \gamma$ transformation is deduced. Movement of only half of the cations is necessary to complete the transformation in either direction and this movement is restricted to a single, filled-empty tetrahedron jump, for each cation. The polymorphisms may be summarised:



An α form may also be prepared at high pressure⁵. Both the β and γ polymorphs have 'tetrahedral structures', that is, the cations and oxygens are all tetrahedrally coordinated. (The α form has an ordered rock-salt structure.)

β -NaFeO₂ and β -NaAlO₂ are isostructural. They have the basic wurtzite structure but with ordering of cations on the tetrahedral sites^{1,2}. This cation ordering causes a lowering of the symmetry from hexagonal P6₃mc in wurtzite to orthorhombic Pbn2₁ in β -NaFeO₂. A schematic (001) projection of the structure (not drawn to scale) is shown in Fig. 1. The unit cell contains two layers of close-packed oxygen atoms at heights 0 and 1/2, and two layers of cations at heights 1/6 and 2/3 (ideally and ignoring differences in cation sizes). The cations for example those at 1/6 are coordinated to three oxygens at 0 and one oxygen at 1/2. Thus, the MO₄ tetrahedra all point upwards, along *z*; linkage of adjacent MO₄ tetrahedra is by corner sharing only (Fig. 2a).

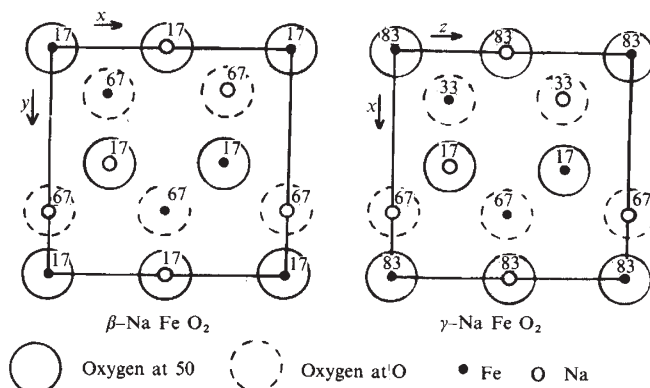


Fig. 1 Schematic projection of β -NaFeO₂ and γ -NaFeO₂ structures. The diagrams are not drawn to scale. Atomic heights, in units of *c*/100 and *b*/100 respectively, are idealised.

The structures of γ -NaAlO₂ and γ -NaFeO₂ have not been determined directly, but they are isostructural with γ -LiAlO₂, tetragonal P4₁2₁2 (ref. 8). The structure of γ -LiAlO₂ was determined independently by X-ray and neutron diffraction on single crystal and powdered specimens, respectively^{7,8}. The structure has been described as a three-dimensional network of linked tetrahedra⁷, its relation to cristobalite, SiO₂, has been noted⁸, and it has been described as a stuffed, distorted cristobalite structure⁸.

I made a model of γ -LiAlO₂ using cardboard tetrahedra and an alternative way of describing its structure became apparent (Figs 1 and 2b). Rather buckled layers of oxygen atoms occur, ideally at 0 and 1/2, which again approximate to hexagonal close packing. The cations are distributed over both sets of available tetrahedral sites; that is, at 1/6, 2/3 and

1/3, 5/6, but only half of the sites in each set are occupied (the set of tetrahedral sites at 1/3, 5/6 in β -NaFeO₂ are empty). The cations at for example 1/3 are coordinated to three oxygens at 1/2 and one oxygen at 0 and so these MO₄ tetrahedra point downwards. The manner of linkage of the tetrahedra is different from that in β -NaFeO₂ in that the tetrahedra occur in pairs. Each NaO₄ tetrahedron shares one edge with an adjacent FeO₄ tetrahedron, and *vice versa*. The remaining linkages are by corner sharing.

The β and γ structures may be classified using the nomenclature of Ho and Douglas⁶: . . . P_A T₊ P_B T₊ P_A . . . for β -NaFeO₂; . . . P_A T₊ T₋ P_B T₊ T₋ P_A . . . for γ -NaFeO₂. P_A P_B P_A . . . refers to anion layers in hexagonal close packing; T₊, T₋ indicate layers of tetrahedral sites which point up and down respectively, and T₋ indicates that only half of the sites in that layer are occupied.

The structural relationship between β -NaFeO₂ and γ -NaFeO₂ is shown in Fig. 1. The oxygen arrangement is the same in both cases and half of the cations, both Na and Fe, occupy similar positions in the two structures. The remaining Na and Fe cations, however, occupy different tetrahedral sites in the β and γ structures.

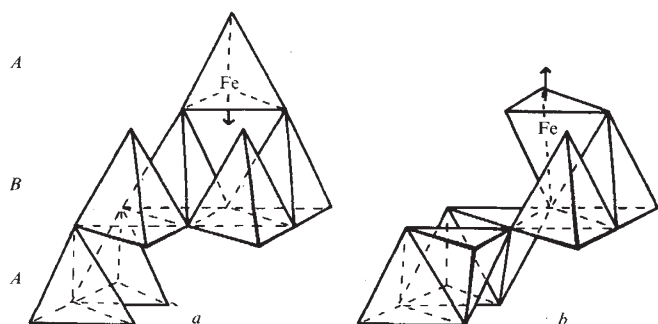


Fig. 2 Schematic structural relationship between β -NaFeO₂(a) and γ -NaFeO₂(b). A, B refer to a hexagonal close-packing sequence.

Closer examination of the structural differences between β and γ forms shows that the $\beta \rightleftharpoons \gamma$ transformation may be effected by a simple topotactic mechanism. Cations at 1/3 in γ -NaFeO₂ can move to 2/3 (as in β -NaFeO₂) simply by jumping through their tetrahedron bases, that is, by passing between the three oxygens at height 1/2 to which they are coordinated. For each cation, the bond to the oxygen at 0 must therefore break and a new bond to the oxygen at 1 will form. Similarly, cations at 5/6 can transform to 1/6 and *vice versa*, by moving through the triangular window of oxygens at height 0. The relationship between the structures, and the mechanism of transformation, are shown in Fig. 2. The β -structure is shown schematically (Fig. 2a), with all of the tetrahedra pointing upwards, as is the corresponding γ structure (Fig. 2b), with half of the tetrahedra pointing upwards and half pointing downwards. The $\gamma \rightarrow \beta$ transformation, written as . . . P_A T₊ T₋ P_B T₊ T₋ P_A . . . \rightarrow . . . P_A T₊ P_B T₊ P_A . . . can be effected simply by inverting those tetrahedra which point downwards (Fig. 2b), and *vice versa* for the $\beta \rightarrow \gamma$ transformation.

Studies on related oxides have revealed several other sets of β , γ type systems. For example, Li₂BeSiO₄ and Li₃PO₄ have low temperature β polymorphs and high temperature γ polymorphs which are related to, but not isostructural with, β and γ -NaFeO₂. Again a close structural relationship exists between the β and γ polymorphs of each pair and a simple topotactic

mechanism can be postulated for the $\beta \rightleftharpoons \gamma$ transformation. These results will be described soon.

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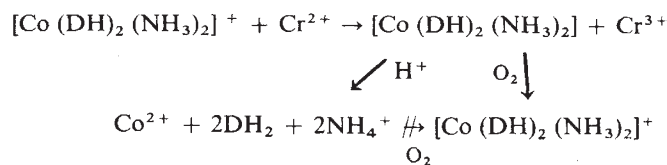
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Cr²⁺-cobaloxime electron transfer reactions

COBALT complexes of dimethylglyoxime (CH₃C:NOH.C: NOH.CH₃), commonly known as cobaloximes, form alkyl derivatives with unusually stable cobalt-carbon bonds^{1,2}. These are regarded by some workers as 'model' compounds for vitamin B₁₂, a biological alkylating agent, the action of which depends on the reversible formation of a similar Co-C bond³⁻⁵. Various mechanisms have been postulated for this reaction⁶. The mechanisms of transalkylation reactions undergone by cobaloximes are thus of great interest; such reactions have been investigated with Hg²⁺ (refs 7 and 8) and with Cr²⁺ (ref. 9). For comparison we are studying the reaction kinetics of other cobaloximes with Cr²⁺. These are apparently electron-transfer reactions¹⁰⁻¹², and should also be considered in the context of the large volume of work that has been done in that field.

Using DH⁻ to represent the mono-anion of dimethylglyoxime, the simple cobaloximes are of the form [Co(DH)₂B₂]⁺, in the case where B is a neutral ligand such as NH₃ or H₂O. Neutral and anionic complexes are well known, with one and two anionic ligands respectively, and the alkyl complexes are usually neutral species of the type [RCo(DH)₂B]. In all cobaloximes the two dimethylglyoximate ions occupy a plane, and are linked by strong hydrogen bonds to form a pseudo-macrocyclic ligand with an N₄ donor set.

We have established that in cases in which both axial ligands are NH₃ molecules, the cobaloxime is reversibly reduced by Cr²⁺:



Cobaloxime(II), the reduced form, was identified by its visible absorption spectrum, and the kinetics of the redox reactions were monitored at 464 nm, where the product absorbs strongly. Cobaloxime(III), regenerated by oxidation of the solution (in air), was isolated as the insoluble perchlorate salt, and microanalysis showed that no chromium was incorporated. In strongly acid solutions (pH < 1), aquation of the reduced species is rapid; this process is acid catalysed and has an equilibrium strongly dependent on [H⁺].