Solid Solution in the FeTiO₅—
TiO₂ System

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The anosovite, or pseudobrookite, form of TiO₂ was early recognised ¹ as being stabilised by Fe, Mg or Al. Subsequent investigations have explored the structural relationships between high (anosovite-like) and low-temperature TiO₂.² In a recent paper, Åsbrink and Magnéli ³ showed that TiO₂ forms continuous, solid solutions with a number of other pseudobrookites, particularly MgTiO₃, Al₂TiO₅ and, apparently, Fe₃TiO₇. Solid solution between Fe₃TiO₇ and Fe₄TiO₈ has also been reported.⁴

Apparently, anomalous lattice parameter behaviour was observed ⁵ in the Fe₃TiO₇—TiO₂ system, in which the c axis parameter, as well as the unit cell volume, increase to a maximum at a 50:50 composition, and then fall again as the composition is altered towards end member TiO₂. The strong reducing power of Ti²⁺ even in TiO₂ suggested that in this system the reaction Ti²⁺ + Fe³⁺ → Ti³⁺ + Fe²⁺ might be taking place, and Mössbauer examination of the system has confirmed that this is so.

At the 50:50 Fe₄TiO₈—TiO₂ composition, which corresponds to the formula Fe₃TiO₇, namely that of ferrous pseudobrookite, the phase present after equilibration in sealed quartz tubes at 1200°C of a compacted mixture of Fe₃TiO₇ and TiO₂ was indeed single phase ferrous pseudobrookite. The Mössbauer spectrum, with isomer shift of 1.328 ± 0.010 mm/sec relative to NBS standard sodium nitroprusside and quadrupole splitting of 3.271 ± 0.010 mm/sec, agrees moderately well with that published for an impure Fe₃TiO₇ and agrees with our own values of 1.329 ± 0.010 mm/sec and 3.167 ± 0.010 mm/sec determined on Fe₄TiO₇, synthesised from a mixture of a reactive synthetic ilmenite FeTiO₃ and anatase form TiO₂. If the Fe₄TiO₇ composition was not rapidly quenched from 1200°C the characteristic Mössbauer spectrum of Fe₄TiO₇ was also observed, in accordance with Haggerty and Lindsay's observation ⁶ that ferrous pseudobrookite disproportionates below 1140°C into a mixture of ilmenite and rutile.

As the TiO₂ content of the starting mixtures was increased beyond the Fe₃TiO₇ composition, creating a solid solution of TiO₂ in Fe₃TiO₇, the tendency to disproportionation rapidly decreased. This paralleled the observations of Lindsay ⁷ on the Fe₄TiO₇—Fe₃TiO₇ system, and our own unpublished observations on the Fe₃TiO₇—MgTiO₃ system. There was no significant change in the Mössbauer parameters as TiO₂ replaced Fe₃TiO₇ in the pseudobrookite structure, with isomer shift 1.319 ± 0.010 mm/sec and quadrupole splitting 3.245 ± 0.010 mm/sec at the composition Fe₆₈Ti₃₂O₇.

We conclude that across the solid solution series created by reacting Fe₄TiO₇ (ferric pseudobrookite) with TiO₂, Ti²⁺ reduces Fe³⁺ to Fe²⁺ and two solid solution series are created. The first is a solution of Fe₄TiO₇ with Fe₃TiO₇ containing no Ti³⁺ and the second, a solution of Fe₃TiO₇ with TiO₂ containing no Fe⁺. For the first series, the lattice parameters obtained by Åsbrink and Magnéli correspond well with those obtained by Akimoto et al.⁸ The mid-composition corresponds to pure ferrous pseudobrookite, which is now seen to form a continuous, solid solution series with TiO₂. The lattice parameter increase as TiO₂ reacts with Fe₃TiO₇ is due to Fe⁺ + Ti⁴⁺ replacing 2Fe³⁺ in the structure, and the decrease in the Fe₄TiO₇—TiO₂ region is due to 2Ti²⁺ replacing Fe⁺ + Ti³⁺, the Fe⁺ ion being by far the largest.⁹

It is interesting to note that TiO₂ stabilizes Fe₄TiO₇ in the same way as TiO₂ in anosovite form is stabilised by what the present results show to be Fe₃TiO₇. This stabilisation of end member pseudobrookite compositions by small additions of other pseudobrookites is a marked feature of this interesting family of compounds, and one which we are further exploring.

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The Vibrational Spectra of 1,1,2-Trichloropropionitrile
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In order to prepare trichloro acrylonitrile we synthesized 1,1,2-trichloropropionitrile CH₂ClCICl₂CN (later called TCPN) as an intermediate product. We have previously reported the vibrational spectra of the related molecules 2-chloro- and 2-bromopropionitrile and found it of interest to study the conformational equilibrium of TCPN. The infrared, Raman and NMR data for this molecule will be reported in the present communication.

Experimental. The sample of TCPN (b.p. 31° at 7 torr) was prepared by chlorinating acrylonitrile and the purity was checked by mass spectrometry and gas chromatography. The compound decomposed upon storage and was distilled immediately before the spectral recordings. However, a few impurity bands were detected in the low temperature infrared spectra.

The infrared and Raman spectrometers and the experimental technique have been described. NMR spectra of TCPN dissolved in CCl₄ and CDCl₄ at 25°, −30° and −60°, using TMS as an internal standard were recorded with a Varian A 60 spectrometer.

Results. The infrared spectra of TCPN as a liquid and as a crystalline solid at ca. −70° are shown in Fig. 1. A complete list of the observed Raman shifts and all except the weakest infrared bands are given in Table 1. Additional infrared spectra of TCPN dissolved in the unpolar CCl₄ and the highly polar CH₂CN were recorded. Significant variations in the intensities of certain infrared bands were observed, those which increase or decrease in polar solvents are denoted i or d in Table 1, respectively. A corresponding variation in the Raman intensities was difficult to observe for this molecule, since most of the appropriate bands were rather weak.

The number of infrared and Raman bands observed for TCPN confirms that the molecule exists in different conformations in the liquid. These are undoubtedly the two staggered conformers having the symmetry C₃ (pseudo trans) and C₁ (pseudo gauche). At least six infrared bands present in the liquid disappeared in the crystalline state. Among them, the bands at 653, 725, and 564 cm⁻¹ definitely were reduced in intensities with polar solvents (d) whereas no corresponding conclusions could be made for those at 1298, 402, and 275 cm⁻¹ because of interfering solvent bands. The C₁-conformer has the higher dipole moment in TCPN and should therefore be stabilized in polar solvents. Accordingly, in agreement with succinonitrile and the 2-halo propionitriles TCPN crystallized in the C₁-conformer at low temperatures. Moreover, as roughly estimated from the relative infrared and Raman band intensities, the C₁-conformer is much more abundant in the liquid TCPN at room temperature than the C₂-conformer. For 2-chloro- and 2-bromopropionitrile on the other hand, the abundance of the two conformers appeared close to the statistical C₁/C₂ = 2:1 ratio in the liquid. Thus for TCPN as well as in the 1,1,2-trihaloethanes, the steric repulsion between the halogens favours the C₁-conformer. Furthermore, a cyano group apparently favours orientation gauche to another cyano group or to a halogen in the crystal, also favouring the C₁-conformer in the crystalline TCPN.

The stronger infrared and Raman bands of TCPN are generally interpreted as fundamentals and are fitted with a description of the atomic motions in Table 1. Apart from the localized group frequencies: CH₂ stretch, CH₂ scissor, and C=N stretch, most of these motions probably involve several atoms. The strong bands at 1214 and 1000 cm⁻¹ are interpreted as overtones in Fermi resonance.

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