

Solid Solution in the FeTi_2O_5 — Ti_3O_5 System

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The anosovite, or pseudobrookite, form of Ti_3O_5 was early recognised¹ as being stabilised by Fe, Mg or Al. Subsequent investigations have explored the structural relationships between high (anosovite-like) and low-temperature Ti_3O_5 .²⁻⁴ In a recent paper, Åsbrink and Magnéli⁵ showed that Ti_3O_5 forms continuous, solid solutions with a number of other pseudobrookites, particularly MgTi_2O_5 , Al_2TiO_5 and, apparently, Fe_2TiO_5 . Solid solution between FeTi_2O_5 and Fe_2TiO_5 has also been reported.⁶

Apparently, anomalous lattice parameter behaviour was observed⁶ in the Fe_2TiO_5 — Ti_3O_5 system, in which the *c* axis parameter, as well as the unit cell volume, increase to a maximum at the 50:50 composition, and then fall again as the composition is altered towards end member Ti_3O_5 . The strong reducing power of Ti^{3+} even in Ti_3O_5 suggested that in this system the reaction $\text{Ti}^{3+} + \text{Fe}^{3+} \rightarrow \text{Ti}^{4+} + \text{Fe}^{2+}$ might be taking place, and Mössbauer examination of the system has confirmed that this is so.

At the 50:50 Fe_2TiO_5 — Ti_3O_5 composition, which corresponds to the formula FeTi_2O_5 , namely that of ferrous pseudobrookite, the phase present after equilibration in sealed quartz tubes at 1200°C of a compacted mixture of Fe_2TiO_5 and Ti_3O_5 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 FeTi_2O_5 ,⁷ and agrees with our own values of 1.329 ± 0.010 mm/sec and 3.167 ± 0.010 mm/sec determined on FeTi_2O_5 , synthesised from a mixture of a reactive synthetic ilmenite FeTiO_3 and anatase form TiO_2 . If the FeTi_2O_5 composition was not rapidly quenched from 1200°C the characteristic Mössbauer spectrum of FeTiO_3 was also observed, in accordance with Haggerty and Lindsley's observation⁸ that ferrous pseudobrookite disproportionates

below 1140°C into a mixture of ilmenite and rutile.

As the Ti_3O_5 content of the starting mixtures was increased beyond the FeTi_2O_5 composition, creating a solid solution of Ti_3O_5 in FeTi_2O_5 , the tendency to disproportionation rapidly decreased. This paralleled the observations of Lindsley⁸ on the FeTi_2O_5 — Fe_2TiO_5 system, and our own unpublished observations on the FeTi_2O_5 — MgTi_2O_5 system. There was no significant change in the Mössbauer parameters as Ti_3O_5 replaced FeTi_2O_5 in the pseudobrookite structure, with isomer shift 1.319 ± 0.010 mm/sec and quadrupole split 3.245 ± 0.010 mm/sec at the composition $\text{Fe}_{0.66}\text{Ti}_{2.33}\text{O}_5$.

We conclude that across the solid solution series created by reacting Fe_2TiO_5 (ferric pseudobrookite) with Ti_3O_5 , Ti^{3+} reduces Fe^{3+} to Fe^{2+} and two solid solution series are created. The first is a solution of Fe_2TiO_5 with FeTi_2O_5 containing no Ti^{3+} and the second, a solution of FeTi_2O_5 with Ti_3O_5 containing no Fe^{3+} . For the first series, the lattice parameters obtained by Åsbrink and Magnéli correspond well with those obtained by Akimoto *et al.*⁶ The mid-composition corresponds to pure ferrous pseudobrookite, which is now seen to form a continuous, solid solution series with Ti_3O_5 . The lattice parameter increase as Ti_3O_5 reacts with Fe_2TiO_5 is due to $\text{Fe}^{2+} + \text{Ti}^{4+}$ replacing 2Fe^{3+} in the structure, and the decrease in the FeTi_2O_5 — Ti_3O_5 region is due to 2Ti^{3+} replacing $\text{Fe}^{2+} + \text{Ti}^{4+}$, the Fe^{2+} ion being by far the largest.⁹

It is interesting to note that Ti_3O_5 stabilizes FeTi_2O_5 in the same way as Ti_3O_5 in anosovite form is stabilised by what the present results show to be FeTi_2O_5 . 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.

1. Zhdanov, G. S. and Rusakov, A. A. *Tr. Inst. Kristallog. Akad. Nauk SSSR* **9** (1954) 165.
2. Åsbrink, S. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1606.
3. Åsbrink, S. and Magnéli, A. *Acta Cryst.* **12** (1959) 575.
4. Iwasaki, H., Bright, N. F. H. and Rowland, J. F. *J. Less Common Metals* **17** (1969) 99.
5. Åsbrink, G. and Magnéli, A. *Acta Chem. Scand.* **21** (1967) 1977.

6. Akimoto, S., Nagata, T. and Katsura, T. *Nature* **179** (1957) 37.
7. Shirane, G., Cox, D. E. and Ruby, S. L. *Phys. Rev.* **125** (1962) 1158.
8. Haggerty, S. E. and Lindsley, D. H. *Carnegie Inst. Washington Yearb.* **68** (1970) P. 247.
9. Shannon, R. D. and Prewitt, C. T. *Acta Cryst. B* **25** (1969) 925.

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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 $\text{CH}_2\text{ClCCl}_2\text{CN}$ (later called TCPN) as an intermediate product. We have previously reported the vibrational spectra of the related molecules 2-chloro- and 2-bromopropionitrile¹ 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 acrylonitrile² 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.³ NMR spectra of TCPN dissolved in CCl_4 and CDCl_3 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 CCl_4 and the highly polar CH_3CN 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 C_s (pseudo *trans*) and C_1 (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 276 cm^{-1} because of interfering solvent bands. The C_1 -conformer has the higher dipole moment in TCPN and should therefore be stabilized in polar solvents. Accordingly, in agreement with succinonitrile⁴ and the 2-halo propionitriles^{1,5} TCPN crystallized in the C_1 -conformer at low temperatures. Moreover, as roughly estimated from the relative infrared and Raman band intensities, the C_1 -conformer is much more abundant in the liquid TCPN at room temperature than the C_s -conformer. For 2-chloro- and 2-bromopropionitrile¹ on the other hand, the abundance of the two conformers appeared close to the statistical $C_1/C_s=2:1$ ratio in the liquid. Thus for TCPN as well as in the 1,1,2-trihaloethanes,⁶ the steric repulsion between the halogens favours the C_1 -conformer. Furthermore, a cyano group apparently favours orientation *gauche* to another cyano group⁴ or to a halogen^{1,5} in the crystal, also favouring the C_1 -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: CH_2 stretch, CH_2 scissor, and $\text{C}\equiv\text{N}$ 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