

a new type of orientation which is not found in the Rh structure. For each set of tetrahedra in the category (2), the fraction (%) of U is indicated in Fig.1, while for each set of tetrahedra in (3), those of U and D are indicated by a set of two numbers, the top indicating the fraction of U and the bottom that of D.

It is notable that the relative locations of Ca, Si, and the oxygen atoms, not bonded to Si, of MI are basically the same with those of Rh and TI (Golovastikov et al., Sov. Phys. Cryst. (1975) 20, 441). The series of phase transitions in C₃S may hence be structurally characterized by the change in mode of orientational order-disorder of the silicate tetrahedra.

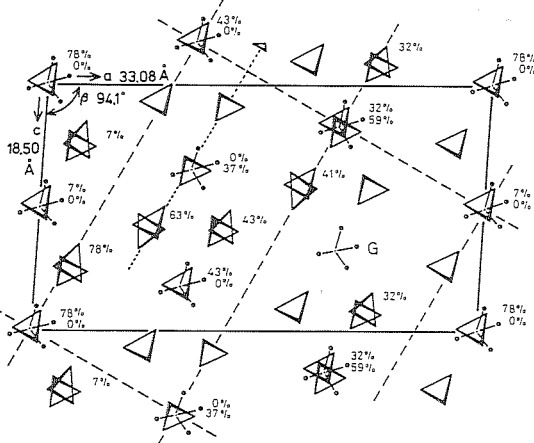


Fig.1 (one of the threefold axes of <MI> is indicated)

08.2-5 NEW PRUSSIAN BLUE-RELATED CYANIDE CRYSTAL STRUCTURES: ONE-, TWO- AND THREEDIMENSIONAL LINKING OF HEXACYANO GROUPS BY HYDRATED CATIONS. By M. Witzel and D. Babel, Sonderforschungsbereich 127 and Fachbereich Chemie der Philipps-Universität, Marburg, Germany

The cyanocomplexes listed in Table I were prepared and characterized by full single crystal structure determinations. The relations to the Fm3m structure types of elpasolites Cs₂LiM(CN)₆ (B.I. Swanson and R.R. Ryan, Inorg. Chem. (1973) 12, 283) and prussian blue (A. Ludi et al., Inorg. Chem. (1970) 9, 2224; (1980) 19, 956) are discussed.

The alkali compounds are elpasolite variants, which contain Rb⁺ or the hydrated ions (Na·H₂O)⁺ or (Li·2H₂O)⁺, resp., in increasingly distorted octahedral N₆ cavities of six surrounding hexacyano groups. The resulting coordination is tetrahedral NaON₃ and LiO₂N₂, resp., for the smaller cations (M. Witzel and D. Babel, Z. Naturf. (1984) 39b, in press).

In the other compounds the M(II) ions Mn and Cd, resp., are octahedrally coordinated by 4H₂O + 2N (trans) in the chain structure of the octahydrate (W. Kurtz and D. Babel, Solid State Commun. (1983) 48, 277) and by 4N + 2H₂O (trans) in the layer structure of the tetrahydrate. In the "trihydrate" structure 1/5 of the M(II) ions have

only square pyramidal N₅-coordination. These ions connect the square meshes of neighbouring layers in turn up and down in the third dimension, to produce a spacious framework. Additional uncoordinated water is hydrogen-bonded within the three structure types, which contrast by well defined and ordered MO_nN_{6-n} octahedra to the disordered species of the prussian blue structures.

Table I:

Compound (A=NMe ₄ ⁺)	S.G.	Z	a(pm)	b(pm)	c(pm)	β(°)
A ₂ RbCo(CN) ₆	I4/m	2	884.7		1233.1	
A ₂ RbFe(CN) ₆	R3m	3	886.7		2149.9	
A ₂ NaFe(CN) ₆ ·H ₂ O	Pnma	4	1863.9	861.7	1317.2	
A ₂ LiFe(CN) ₆ ·2H ₂ O	C2/c	4	1712.8	876.0	1625.4	119.3
ACdFe(CN) ₆ ·3,2H ₂ O	I4	10	1650.6		1725.7	
AMnMn(CN) ₆ ·3,2H ₂ O	I4	10	1653.2		1728.8	
AMnCr(CN) ₆ ·4H ₂ O	Pnma	4	1491.0	785.5	1723.5	
AMnCo(CN) ₆ ·8H ₂ O	P4/n	2	1062.2		1046.2	

08.2-6 NEW METASTABLE TELLURIUM OXIDE PHASES WITH HIGHLY DISORDERED CaF₂ STRUCTURES
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By quenching SrO-TeO₂ melts, SrTe₅O₁₁ is formed, in which the heavy atoms are distributed at random among the metal positions of a CaF₂ structure with incomplete oxygen packing (H.-G. Burckhardt, M.Trömel, Acta Cryst. (1983) C39, 1322). Extraordinarily high apparent temperature factors are due to large irregular displacements of all atoms. This kind of disorder (undefined short range order in spite of highly symmetrical long range order) results from tellurium being placed in a CaF₂-type oxide which does not meet the geometrical requirements of the Te(IV) coordination. Similar phases are formed from TeO₂ and oxides of divalent and trivalent metals with ionic radii between 0.93 and 1.21 Å (Pb, Y, La, lanthanides). Their lattice constants (Å) and approximate formulae are:

SrTe ₅ O ₁₁	5.655	Gd ₂ Te ₆ O ₁₅	5.611
PbTe ₃ O ₇	5.647	Tb ₂ Te ₆ O ₁₅	5.600
Y ₂ Te ₆ O ₁₅	5.586	Dy ₂ Te ₆ O ₁₅	5.587
La ₂ Te ₆ O ₁₅	5.695	Ho ₂ Te ₆ O ₁₅	5.575
Pr ₂ Te ₆ O ₁₅	5.668	Er ₂ Te ₆ O ₁₅	5.567
Nd ₂ Te ₆ O ₁₅	5.655	Tm ₂ Te ₆ O ₁₅	5.551
Sm ₂ Te ₆ O ₁₅	5.638	Yb ₂ Te ₆ O ₁₅	5.537
Eu ₂ Te ₆ O ₁₅	5.617	Lu ₄ Te ₇ O ₂₀	5.491

CeTe₆O_(14-x) (a = 5.675 Å) is partly reduced when prepared from CeO₂ and TeO₂. All phases decompose between 300 and 600 °C, forming stable crystalline compounds.