20.4-2 MODULATED PHASES IN THE Ca_2SiO_4-Ba_2SiO_4 SYSTEM. By R.L. Withers, J.G. Thompson and B.G. Hyde, Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, ACT 2601, Australia.

Compounds of the A_2BX_4 family have long been of interest to the crystal chemist. This is due in no small measure to the sheer size and variety of the family, to their flexibility in forming solid solutions and to the numerous different polymorphs and complicated sequences of phase transitions they sometimes exhibit as a function of temperature (Tuinstra, F. and van den Berg, A.J., Phase Transitions, 1983, 3, 275-282; Eysel, W., Hofer, H.H., Keester, K.L. and Hahn, Th., Acta Cryst. 1985, B41, 5-11). For most A_2BX_4 compounds, there are essentially only two distinct structure types or parent structures - a high temperature, 'hexagonal' form isomorphous to α-K_2SO_4 and a lower temperature, orthorhombic form isomorphous to β-K_2SO_4. In addition, however, polymorphs often exist which are best described as weakly distorted or modulated variants of one or other of these two parent structures. Such modulated structures are generally characterized by weak satellite reflections flanking the Bragg reflections of the parent structure and are easily missed by conventional X-ray diffraction counter techniques. Our initial interest was in looking for such modulated phases of Ca_2SiO_4 by means of electron diffraction. As conventional electron microscope hot stages are not capable of attaining the temperatures necessary to observe the high temperature polymorphs, we employed the doping method of Suzuki and Yamaguchi (Suzuki, K. and Yamaguchi, G., Proc. of the Fifth International Symposium on the Chemistry of Cement. Tokyo, 1968, 67-73) to "quench" both the α and α' forms. The resultant electron diffraction patterns showed that the $Ca_{2-x}Ba_xSiO_4$ structures thus obtained were not as simple as previously reported, but were, in fact, extensively modulated. This led us to investigate the Ba_2SiO_4-Ca_2SiO_4 phase diagram (Matkovic, B., Popovic, S., and Grzeta, B., J. Am. Ceram. Soc., 69, 1986, 132-134). Five distinct types of modulated phases (α_m, Q, X, α_L' and T) were found, each with a characteristic set of satellite reflections. The characteristic extinction conditions associated with each set is used to deduce the way in which the parent structures are distorted to produce the modulated variants.

20.4-3 GEOMETRICAL MODELS OF FLUORITE-RELATED SUPERSTRUCTURES AS AIDS TO STRUCTURE DETERMINATION. THE STRUCTURE OF Ca_2YbF_7. By D.J.M. Bevan, S.E. Lawton, M.J. McCall and M.R. Taylor, School of Physical Sciences, Flinders University of South Aust. and H.J. Rossell, CSIRO Division of Materials Science, Melbourne, Aust.

The solution of the structure of the mineral tveitite - $Ca_{14}Y_5F_{43}$ (D.J.M. Bevan, J. Strähle and O. Greis, J.Solid State Chem., 1982, 44, 75-81) led to the recognition of a new structural principle (D.J.M. Bevan, O. Greis and J. Strähle, Acta Cryst., 1980, A36, 889-891) for anion-excess superstructures. As in all fluorite-related structures, the cation array remains as essentially unaltered f.c.c., and it is the anion arrangement which is varied. The fundamental step in this process is the conversion of X_8 anion cubes in fluorite to X_8 anion square antiprisms. More specifically, the fluorite element (M_6X_{32}) of six MX_8 cubes sharing edges to enclose an empty X_8 cube is converted to a cluster of six MX_8 square antiprisms sharing corners to enclose an empty cuboctahedron. This can be presented by: $M_6X_{32} + 4X \longrightarrow M_6X_{36}$, and if an additional anion is accommodated at the centre of the cuboctahedron, the cluster becomes M_6X_{37}.

This cluster principle has now been used widely in new descriptions of known structures, and in constructing models of unknown structures. This latter enterprise has been outstandingly successful and has led to the experimental determination of previously unknown structures, e.g. Ca_2YbF_7 and β-U_4O_{9-y} (D.J.M. Bevan, I.E. Grey and B.T.M. Willis, J. Solid State Chem., 1986, 61, 1-7). Moreover, the ideal geometrical models closely approximate the real structures where these are known (D.J.M. Bevan and S.E. Lawton, Acta Cryst., 1986, B42, 55-58). Models of different cluster arrangements in the structures of the Greis series R_nF_{2n+5} (R = rare-earth), are shown, and the X-ray structure analysis of Ca_2YbF_7 is described.

20.4-4 X-RAY ANALYSIS OF METALLIC SUPERLATTICES WITH SINGLE CRYSTAL TECHNIQUES. By R.H.M. van de Leur, J. te Nijenhuis and F.Tuinstra, Department of Applied Physics, University of Technology, Delft, The Netherlands.

Superlattices of Nb/V and Ta/V have been grown with a controlled sinusoidal occupation modulation .The substrate was a sapphire (012) surface, the growth direction was the (001) direction of the bcc average lattice. Because of the difference of the atomic size of the constituents, substitutional as well as displacive modulation is present. Modulation periods ranged from 7Å up to 130Å. Due to the highly oriented epitaxial growth the diffraction patterns of these superlattices are similar to single crystal patterns. This offers the opportunity to use a single crystal four circle diffractometer for the diffraction data collection. A special scanning procedure was developed in order to study independently the variation in the modulation wave vector and the variation in the orientation of the average bcc lattice. Of about 40 main- and satellite reflections positions and intensities were measured. Apart from the usual ω-scans a scanprocedure was applied in which a reciprocal lattice site of the bcc lattice acts as the origin for a scan of its satellite reflections.These special scans were both of the ω-type and of the ω-2θ-type. From these data the average structure, the modulation period, the form and the amplitude of the modulation function have been determined. The modulation functions induced by the periodic growth conditions in the Nb/V and the Ta/V samples were intended to be pure sine functions. The structure analysis proved that the actual structures fulfilled these expectations.