**20.4—3　　DETECTION OF MODULATED STRUCTURE IN PROUSTITE;** By S.S. Khasanov, V.Sh. Shekhtman, I.M. Shmytko, Institute of Solid State Physics, 142432, Chernogolovka, USSR

It has been found (see P.J.S.Ewen, W.Taylor and G.L.Paul, J.Phys.C: Solid State Phys., 16, (1983) 6475—6490) that at 28 K the trigonal proustite crystals (Ag_3AsS_3) undergo the first order transition into the ferroelectric phase accompanied with the symmetry decrease up to the triclinic. It is also known that near 60 K noticeable anomalies of physical properties of proustite are observed. It is supposed to be due to the second order transition. The present paper deals with the X-ray study of proustite in the region of 60 K.

The results of this paper unambiguously evidence that below 60 K a modulated structure is formed in the proustite crystal. Each reflection of parent structure seen in the oscillating-crystal photographs taken below 60 K is surrounded by several marked satellite reflections (six in the general case), which are absent above 60 K. Below 28 K these satellites also disappear due to the phase transition occuring at this temperature. The diffraction pattern observed in the temperature range 28—60 K can be explained only by the onset of structure modulations along the appropriate directions. As the analysis of the satellite reflection arrangment shows, their related modulation wave vectors are oriented along the symmetrical directions $[\bar{1}0.1]^*$, $[01.1]^*$, $[\bar{1}1.1]^*$ of the reciprocal space, the magnitude of any vectors being approximately 1/3 of the distance between the reciprocal lattice points in the corresponding direction. Precision measurements of the
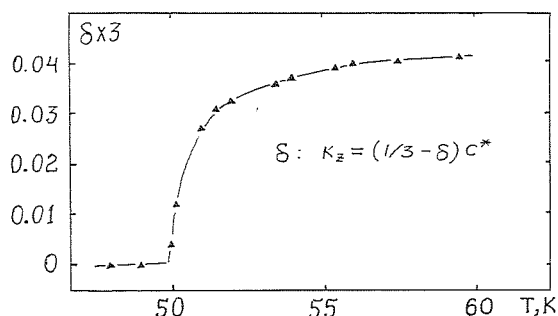
modulation wave vectors enabled us to establish the incommensurability of modulation in the temperature range 50—60 K and to reveal incommensurate-commensurate transition at 50K. The modulation wave vector component along the polar C-axis of crystal is commensurate and equals 1/3 c^* at temperatures below 50 K. Above this temperature it becomes incommensurate. The figure shows temperature dependence of the parameter δ wich characterizes the incommensurate wave number $K_c = (1/3 - \delta) c^*$. The basal plane component remains constant and equals 1/3 a^*.

Thus, the direct diffraction experiment has revealed the modulated structure in proustite. It has been shown that in the region of 60 K Ag_3AsS_3 crystals undergo successive phase transitions: symmetric phase $\xleftarrow{60K}$ incommensurate phase $\xleftarrow{50K}$ commensurate phase.

20.4—4　　INCOMMENSURATE PHASE AND SUPERLATTICE OF $LiKSO_4$. By Xie Si-shen, Liang Jing-kui and Li Yin-yuan. Institute of Physics, Academia Sinica, BEIJING, China.

The phase transition of $LiKSO_4$ above RT have been investigated by means of X-ray powder diffraction and thermal analysis (DTA and DSC). The X-ray diffraction patterns were taken with a Guinier-Lenne camera at the temperatures 695°C, 690°C, 540°C, 470°C, 440°C, 370°C and RT. It is established that the crystal structure of $LiKSO_4$ between the melting point and 675°C is isomorphous to α-K_2SO_4, its possible space group being $P6_3/mmc$. Cooling below T_i=675°C, there occurs the modulated structure, which is analogous to the incommensurat phase in K_2WO_4, K_2MoO_4, ..., and the parameter changes with the temperature from 0.492(640℃) to 0.500(470℃). At 470℃ I---C phase transition (lock-in) takes plase, after which the crystal structure becomes the superlattice of the RT phase ($P6_3$). The unit cell of the superlattice is 4 times larger than that of RT structure with a'=2a and c'=c. At 439°C the superlattice disapears with the release of latent heat. No incommensurate phase is found below RT.

20.4—5　　THE MODULATED STRUCTURE OF $NbTe_4$.

By H. Böhm and H.G. v. Schnering, Max-Plank-Institut für Festkörperforschung, Stuttgart, FR-Germany.

The tetragonal structure of $NbTe_4$ has been determined by Selte and Kjekshus (Acta. Chem.-Scand. (1964) 18, 690). The Nb-atoms occupy the centers of tetragonal antiprisms of tellurium. These authors did not consider the week satellite reflections, which are observed along c^* and which require a doubling of the a-axis and an approximate trippling of the c-axis.

Own measurements confirm that the period of the modulation along c and the period of the average structure are not commensurate; for the period of the modulation a value of M=3.20(5)c has been determined. The basic structure is discussed in a C-centered setting. In order to use existing refinement programs the structure has been treated as a threefold superstructure (M=3).

The refinement calculations show, that in the tetragonal basic structure the Nb-atoms are modulated along c according to a longitudinal wave. The squares of the Te-atoms are affected by three modes : a longitudinal mode along c, transversal shifts of the atoms according to a "breathing mode" and a libratior about the c-axis. By the longitudinal wave a sequence of Nb_3-groups, Nb_2-pairs and isolated Nb-atoms is formed.

The wave affecting the atoms in the column at (0,0,z) and the one affecting the atoms at (1/2,1/2,z) in the C-centered setting have a phase shift close to π.

By the "breathing mode" a sequence of large and small Te-squares is formed in such a way that a big Te-square is located between two Nb atoms of short bond distance and a smaller Te square is formed when the Nb-atoms are further apart. By the oscillatory motion of the libration mode Te-Te pair bonds occur between Te atoms of different antiprisms about $(0,0,z)$ and about $(1/2,1/2,z)$. The bond lengths vary between $2.90(1)$ Å and $2.95(1)$ Å. In the Nb-chain along c the bond lengths vary between $3.08(1)$ Å for a Nb-Nb pair and 3.96 Å between Nb_3-groups.

By the refinement calculations in the space-group P4 the following R-values have been obtained : R=0.062 for the modulated structure (1024 unique reflections), R=0.062 for the average structure (290 unique main reflections) and R=0.046 for the complement structure (734 unique satellite reflections).

The scale factor has been refined by the main reflections (average structure), whereas, the atomic shifts have been determined by the satellite reflections alone (complement structure).

The evaluation of the Patterson-function as well as a Fourier-synthesis confirm the obtained results.

TABLE

Space groups	Type of modulation	main reflections R_M	R-indices satellites R_S	common R
$P^I {}_{\bar{1}s1}^{mmm}$	occupational	0.0611	0.1617	0.0894
$P^I {}_{ss1}^{2mm}$		0.0619	0.1380	0.0833
$P^I {}_{\bar{1}s1}^{mmm}$	mixed	0.0553	0.0908	0.0653
$P^I {}_{ss1}^{2mm}$		0.0555	0.0822	0.0630

The improvement due to the superposed displacive wave (displacement of ions along y, only) is evident. The difference between the two space groups, solves the pr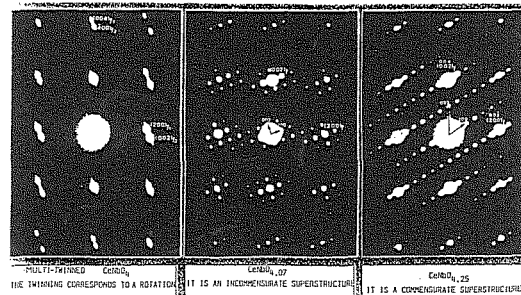oblem of phase shifts between the modulating waves. Contrary to $P^I {}_{ss1}^{2mm}$, the $P^I {}_{\bar{1}s1}^{mmm}$ group excludes all relative phase shifts between the individual waves. The phase shifts, however, do exist as indicated by the significant lowering of R_S index (see Table). The occupational wave of NO_2 group is shifted in respect to Na^+ ion wave by about $22°$. There are practically no phase shifts between the individual displacive and occupational waves. The amplitude of the displacive wave of Na^+ was found almost two times as big as that of NO_2, with the occupational amplitudes being approximately the same.

20.4—6   RE-EXAMINATION OF THE MODULATED STRUCTURE OF THE $NaNO_2$ IN ANTIFERROELECTRIC PHASE.

By W.A. Paciorek and D. Kucharczyk, Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland.

The structure of the antiferroelectric phase of $NaNO_2$ has been refined (Kucharczyk et al., Ferroelectric (1978) 21, 445) for a mixed occupational and displacive modulation model. This was later supported by theorethical studies (Michel, Phys. Rev. B (1981) 24, 3998; Mc Connell & Heine, Phys. Rev. Lett. (1981) 46, 1091). However, due to a number of simplifications concerning the symmetry treatment, the refinement procedure and some arbitraryness in phase relationships of the modulating waves, the obtained structure is no longer the good base for more detailed studies. We decided, therefore, to reinvestigate this structure by applying the recently developed approach to modulated structure determination. The special least squares program for modulated structures refinement by use of $(3+1)$-dimensional symmetry (de Wolff et al., Acta Cryst. (1981) A37, 625) has been written by one of us (W.A.P.). The refinement was carried out in two superspace groups (see Table) with a data set of 214 reflections (seven of them removed due to extinction reasons). At the begining, in addition to positional and anisotropic thermal parameters, only the individual occupational waves were taken into account. Next, all the possible displacive waves were added. However, the components of the displacive waves along x and z were proved negligibly small and consequently set to zero. Furthermore, the rigid body like behaviour of NO_2 group was detected and for the final refinement all modulation parameters of the N and O atoms, were constrained. The final discrepancy indices obtained for different space groups for pure occupational and mixed modulation are as follows:

20.4—7   ANION INSERTION IN THE COMMENSURATE-INCOMMENSURATE FERGUSONITE-LIKE PHASES $CeNbO_{4+x}$.

By J.L. Hodeau and M. Marezio, Laboratoire de Cristallographie. C.N.R.S., associé à l'U.S.M.G., 38042 Grenoble-Cedex, France, and R.S. Roth, National Measurements Laboratory, N.B.S. Washington, D.C. 20234, U.S.A.

The compound $CeNbO_4$ can be oxidized at relatively low temperatures ($\sim 600°C$), the reaction products are discrete compounds $CeNbO_{4+x}$, x = 0.07, 0.25, 0.33. X-ray, electron diffraction and electron microscopy results on the two first compounds are reported :

MULTI-TWINNED $CeNbO_4$ $CeNbO_{4.07}$ $CeNbO_{4.25}$
THE TWINNING CORRESPONDS TO A ROTATION   IT IS AN INCOMMENSURATE SUPERSTRUCTURE   IT IS A COMMENSURATE SUPERSTRUCTURE

Commensurate phase $CeNbO_{4.25}$

The supercell is 12 times that of the fergusonite. Its structure was determined by X-ray diffraction. The anion insertion mechanism corresponds to a rotation of one edge of the oxygen tetrahedra around some of the niobium atoms. The compression of the anion framework resembles that of Vernier structures. Oxygen clusters containing 3 extra anions are formed. The cation displacement are rather small. however, the anion clusters are located close to those zones of the crystal where the cation displacements are larger. The final values of the R fac-