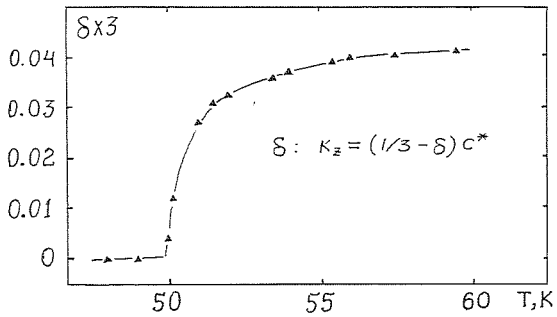
20.4–3 DETECTION OF MODULATED STRUCTURE IN PROUSTITE; By S.S. Khasanov, V.Sh. Shekhtman, I.M. Shmytko, Institute of Solid State Physics, 142432, Chernogolovka, USSR

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°C) to 0.500(470°C). At 470°C 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.