05.1—59   X-RAY STUDY OF THE PHASE TRANSITION IN TETRACENE   U. Sondermann*, A. Kutoglu* and H. Bässler+, *Institut für Mineralogie, Petrologie, Kristallographie, +Fachbereich Physikalische Chemie, Universität Marburg, D 3550 Marburg, BRD

The triclinic crystal structure of tetracene appears to be thermodynamically less stable than the monoclinic phases of its lower homologs. Below 180K it is supposed to undergo a structural transition not yet identified by diffraction methods. The transition often causes crystal shattering and is accompanied by an increase in intermolecular coupling as evidenced by both a redshift of the optical absorption and a significant increase of the Davydov-splitting. The transition temperature is poorly defined. Depending on parameters like crystal mounting or perfection it can vary between 20K and 180K. The lack of structural information prompted us to conduct a systematic X-ray study.
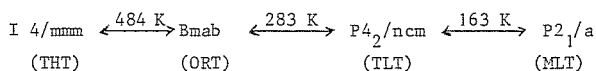An otherwise extensively studied crystal with a transition near 160K was investigated by powder and single crystal methods in a temperature range 77K <T <360K. All standard techniques for handling samples completely failed. Finally, we succeed to observe the transition by mounting the samples in a strainless manner. The transition temperature of a sample is smeared out. A few samples change in the whole, others step by step; while some show their transition only in domains. The low temperature phase is triclinic like that for room temperature which is determined by Campbell et al. (Acta Cryst (1962)15,289). The main characteristic feature of the observed transition seems to be the distinct change in cell angle α.
The experiments and their results will be presented. The transition will be explained by a sudden turn over of the molecules in the cell, which essentially influences the intermolecular coupling. The intensity change of the Bragg-peaks in the transition range give evidence for incommensurable lattice behaviour.

directions while, apparently, no correlation exists along c. Hence each layer can be considered as a mosaic of ordered "clusters" involving a hundred or so $CdCl_6$ octahedra; disorder along $\vec{c}$ results from the absence of coherence in the stacking of these "clusters" from one layer to the next ones. These "clusters" correspond to a local distorsion of the $CdCl_6$ layers, and the mean configuration of the octahedra arrangement, which is described by the Bmab or $P4_2/ncm$ space group in the ORT or TLT phase, respectively, in fact corresponds to a time and space-averaged structure.

On going into the MLT phase, the diffuse scattering patterns disappear, as expected for an ordered phase. X-Ray diffuse scattering results clearly show the existence of two-dimensional short range correlations in the disordered ORT and TLT phases of $(CH_3NH_3)_2$ $CdCl_4$ and then confirm that such local distorsion of the crystal lattice were indeed evidenced by Raman spectroscopy.

06.1—60   PHASE TRANSITIONS IN THE PEROVSKITE-TYPE LAYER COMPOUND $(CH_3NH_3)_2CdCl_4$: EVIDENCE OF TWO-DIMENSIONAL SHORT-RANGE CORRELATIONS. By N.B.Chanh* M.Couzi, Y.Haget*, C.Hauw*, A.Meresse* and R.Mokhlisse***

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$(CH_3NH_3)_2$ $CdCl_4$ belongs to the family of perovskite type layer compounds, built up from infinite layers of cornersharing $CdCl_6$ octahedra with the $CH_3NH_3^+$ cations occupying the cavities between octahedra. This compound exhibits a number of structural phase transitions (G.Chapuis et al, Phys.Stat.Sol. (a) (1975), 31, 449 and (1976) 36, 285), as indicated below :

I 4/mmm $\xleftrightarrow{484 \text{ K}}$ Bmab $\xleftrightarrow{283 \text{ K}}$ $P4_2$/ncm $\xleftrightarrow{163 \text{ K}}$ $P2_1$/a

(THT)   (ORT)   (TLT)   (MLT)

In all phases, but the monoclinic one stable at low temperature (MLT), the $CH_3NH_3^+$ groups exhibit orientational disorder of dynamic nature. The Raman spectra obtained in the disordered ORT and TLT phases revealed the presence of low lying overdamped modes assigned to $CdCl_6$ octahedra motions; the unusual behaviour of these modes was tentatively imputed to the existence of disorder involving not only the $CH_3NH_3^+$ cations, but also the $CdCl_6$ octahedra (R.Mokhlisse et al.,J.Phys.C., (1983), 16,1367).

X-ray diffuse scattering patterns are clearly evidenced in the disordered ORT and TLT phases; they consist in diffuse streaks parallel to the $\vec{c}*$ direction (here $\vec{c}$ designates the direction perpendicular to the layer planes). The shape and spatial distribution of the streaks are in agreement with a simple model of planar disorder involving the $CdCl_6$ octahedra layers. Correlation lenghts of about 6 to 8 unit cells are determined in the $\vec{a}$ and $\vec{b}$

05.1—61   CATIONS DISTRIBUTION IN GLASERITES.
By B.N. Mehrotra,* Institut für Kristallographie, Technische Hochscule, Aachen, Germany.

Glaserites are formed by combining large ($1.3A^\circ$ or more) and medium ($1A^\circ$ or less) sized cations with tetrahedral framework, e.g. $K_3Na(SO_4)_2$ etc. Mehrotra et al (3). Glaserites crystallize with one of the following structures:

1. $P\bar{3}$ 2/m 1, P3 2/c 1
2. Cl 2/m, Cl ml, Cl 2 1, Cl 2/c, Cl c 1.

The structure of $K_3Na(SO_4)_2$ glaserites have been studied by Gossner (2) and Bellanca (1). Our structure determination and refinement with R = 0.085 (others have not refined the structure) gives the following parameters.

Space group no. 164, $P\bar{3}$ 2/m 1.

Table 1. Position and thermal parameter

Atom	x	y	z	B
Na	0	0	.5	2.88(5)
K_1	0	0	0	3.86(5)
K_2	.3333	.6666	.6841(9)	1.09(1)
S	.3333	.6666	.2334(10)	0.83(13)
O_1	.3333	.6666	.0169(26)	0.27(2)
O_2	.186(5)	-.186(5)	.3039(26)	4.0(5)

Table 2. Bond lengths and angles

S – O	O – S – O	O – O
1.578x1	109.58x3	2.543x3
1.534x3	109.36x3	2.504x3

To keep the thermal parameter and the tetrahedron bond lengths to a reasonable value, the following models (ordered and disordered) are proposed:

Table 3

Atom	Coordinate	Gossner Model	Bellanca Model	Ordered Model (This work)	Disordered Model
M_1	000	Na	Na	KNa	KNa
M_2	$00\frac{1}{2}$	K	Na	KNa	KNa
M_3	$\frac{1}{3}\ \frac{2}{3}\ z$	K	K	K	KNa

M: Metal atom Na, K or KNa.

Three glaserites $K_3Na(SO_4)_2$; $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2-((K_3Na(SeO_4)_2$ have super structures along c-axis, Mehrotra (4)), and are presently under investigation on the basis of ordered and disordered models.

References:
1. Bellanca, A. (1943), Periodicodi mineralogia 14, 69–97.
2. Gossner, B. (1928), Neues Jahrh. Miner. 57A.
3. Mehrotra, B.N.; Eysel, W. & Hahn, Th. (1977) Acta Cryst. B33, 305–306.
4. Mehrotra, B.N. (1977), N. Jh. Miner. Mh., 9, 398–407.

05.1–62   LOW TEMPERATURE STRUCTURAL TRANSFORMATIONS IN THE $Pb_{1-x}Sn_xSe$ SYSTEM. By V.I.Ivanov, V.Sh.Shekhtman, I.M.Shmytko, Solid State Physics Institute of the USSR Academy of Sciences, 142432 Chernogolovka, USSR

A precision investigation has been carried out of the temperature dependence of interplanar spacings of the $Pb_{1-x}Sn_xSe$ narrow-band semiconductor system (x=0,37; 0,42; 0,43) (I.M.Shmytko et.all., Solid State Physics, vol.22, N5, 1384, 1980). Structure transitions of the first order have been observed at 170K and 260K for x=0,42 and x=0,43, respectively, the hysteresis being 80K. The phase transitions are accompanied with the symmetry decrease, $Fcub \rightarrow P_{ortho}$ and are based on the cubic lattice twinning along the system (010)/(001). The orthorhombic phase unit cell parameters at T=255 K are: a=11,694 A, b=4,473 A, c=4,191 A. The low temperature phase is realized in the form of developed "parquet" systems with the following orientation relations [100]cub // [100]$ortho$; [011]cub //[010]$ortho$; [011]cub // [001]$ortho$.

Phase transition for x=0,37 has not been observed. Precision measurements of $d = d(T)$ have, however, revealed the anomalies in the temperature dependence of the lattice parameter within the temperature range 215–250 K, depending on composition. The anomalies observed are related to the evolution of the narrowband semiconductor phonon spectrum in the temperature regions corresponding to the valence band-conduction band inversion (L.K.Vodopianov, I.V.Kutcherenko et. al., Letters in JETF, 27, 101, 1978).

05.1–63   THE ROLE OF B SITE CATION DISORDER IN DIFFUSE TRANSITION BEHAVIOUR OF $Pb(In_{1/2}Nb_{1/2})O_3$ PEROVSKITE FERROELECTRIC By P.Groves and A.M.Glazer, Clarendon Laboratory, University of Oxford, Parks Road, Oxford, OX1 3PU, U.K.

In $Pb(In_{1/2}Nb_{1/2})O_3$ the degree of order of the In^{+3} and Nb^{+5} cations in the B sites of the structure can be controlled by suitable thermal annealing. For samples which have been well ordered by annealing for a long time, it is found that single crystals show a first order ferroelectric phase transition from dielectric measurements. With increasing disorder, the crystals exhibit the classical diffuse phase transition typical of a ferroelectric relaxor, with a broad Curie range and strong low-frequency dielectric Debye relaxation in the transition range. Single-crystal X-ray diffraction measurements of the size of the ordered microregions, and of the degree of order are presented for different annealing times. A series of semi-continuous, high-temperature, single-crystal X-ray diffraction photographs, show how the character of the transition changes with prolonged heat treatment. The Curie temperature T_c, increases with annealing time following an exponential law.

05.1–64   THE CHANGE IN SYMMETRY AT THE I-II PHASE TRANSITION IN DICALCIUM BARIUM PROPIONATE. By S. Singh, Allen Clark Research Centre, Plessey Research Centre, Plessey Research Ltd., Caswell, Towcester, Northants., U.K. and F. R. Wondre, Clarendon Laboratory, Oxford University, Parks Road, Oxford OX1 3PU, U.K.

Dicalcium barium propionate, $Ca_2Ba(C_2H_5COO)_6$ undergoes two phase transitions at atmospheric pressure: the I-II, first order transition at approximately 267K and the II-III transition at 240K. The symmetry of the low temperature phase II has been characterised by X-ray diffraction methods and has space group Pnma or $Pn2_1a$. Powder and single crystal techniques have been used to explain the formation of two kinds of twins, present in phase II, in terms of the phase I lattice. Lattice parameters have been determined in the temperature region of 125K to 300K. The symmetry of phase III was investigated. The relationship between dicalcium barium propionate, DBP and dicalcium barium acrylate, DBA is discussed.