

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.

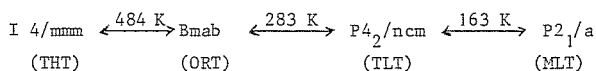
An otherwise extensively studied crystal with a transition near 160K was investigated by powder and single crystal methods in a temperature range 77K < T < 360K. All standard techniques for handling samples completely failed. Finally, we succeed to observe the transition by mounting the samples in a 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  $\alpha$ .

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.

06.1-60 PHASE TRANSITIONS IN THE PEROVSKITE-TYPE LAYER COMPOUND  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ : 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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$(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$  belongs to the family of perovskite type layer compounds, built up from infinite layers of corner-sharing  $\text{CdCl}_6$  octahedra with the  $\text{CH}_3\text{NH}_3^+$  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 :



In all phases, but the monoclinic one stable at low temperature (MLT), the  $\text{CH}_3\text{NH}_3^+$  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  $\text{CdCl}_6$  octahedra motions; the unusual behaviour of these modes was tentatively imputed to the existence of disorder involving not only the  $\text{CH}_3\text{NH}_3^+$  cations, but also the  $\text{CdCl}_6$  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  $\text{CdCl}_6$  octahedra layers. Correlation lengths of about 6 to 8 unit cells are determined in the  $\vec{a}$  and  $\vec{b}$

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  $\text{CdCl}_6$  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 distortion of the  $\text{CdCl}_6$  layers, and the mean configuration of the octahedra arrangement, which is described by the Bmab or  $\text{P4}_2/\text{ncm}$  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  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$  and then confirm that such local distortion of the crystal lattice were indeed evidenced by Raman spectroscopy.

05.1-61 CATIONS DISTRIBUTION IN GLASERITES. By B.N. Mehrotra\*, Institut für Kristallographie, Technische Hochschule, Aachen, Germany.

Glaserites are formed by combining large ( $1.3\text{\AA}^0$  or more) and medium ( $1\text{\AA}^0$  or less) sized cations with tetrahedral framework, e.g.  $\text{K}_3\text{Na}(\text{SO}_4)_2$  etc. Mehrotra et al (3). Glaserites crystallize with one of the following structures:

1.  $\text{P}\bar{3} 2/\text{m } 1, \text{P3 } 2/\text{c } 1$
2.  $\text{C1 } 2/\text{m}, \text{C1 } \text{m}1, \text{C1 } 2 1, \text{C1 } 2/\text{c}, \text{C1 } \text{c } 1.$

The structure of  $\text{K}_3\text{Na}(\text{SO}_4)_2$  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,  $\text{P}\bar{3} 2/\text{m } 1.$

Table 1. Position and thermal parameter

| Atom         | x       | y        | z         | B        |
|--------------|---------|----------|-----------|----------|
| Na           | 0       | 0        | .5        | 2.88(5)  |
| $\text{K}_1$ | 0       | 0        | 0         | 3.86(5)  |
| $\text{K}_2$ | .3333   | .6666    | .6841(9)  | 1.09(1)  |
| S            | .3333   | .6666    | .2334(10) | 0.83(13) |
| $\text{O}_1$ | .3333   | .6666    | .0169(26) | 0.27(2)  |
| $\text{O}_2$ | .186(5) | -.186(5) | .3039(26) | 4.0(5)   |