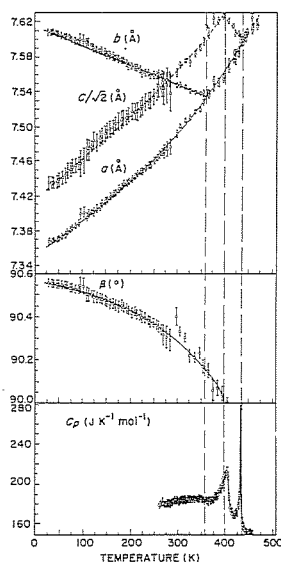


05.1-76 SOFT MODES AND ELASTIC STRAIN AT THE TETRAGONAL-TO-MONOCLINIC PHASE TRANSITION IN ANTIFLUORITE AND RELATED STRUCTURES. By J. Ihringer and S. C. Abrahams, AT&T Bell Laboratories, Murray Hill, NJ 07974, USA.

The phase transition from $P4/mnc$ to $P2_1/n$ in the antifluorite K_2TeBr_6 is shown, by X-ray and heat capacity measurement, to undergo two independent strain-coupled processes. The angle β between the a - and c -axes in the tetragonal phase increases sharply from 90° at about 400K, on cooling, the temperature at which the thermal expansivity of the c -axis changes sign, see figure below [Abrahams, Ihringer, Marsh & Nassau (1984). To be published]. Further cooling to 359K breaks the identity of the a - and b -axial lengths. Mode analysis of the antifluorite structure in $P4/mnc$ at the zone center shows that one E_g basis vector reduces the symmetry to $P2_1/n$. Two order parameters Q_D and Q_R of identical symmetry, defined respectively as the displacement of the K^+ ion in the $[010]$ direction from the tetragonal $4d$ special position and the cooperative rotation about the tetragonal $[010]$ of the $TeBr_6^{2-}$ octahedra at the phase transition, are shown to follow an identical critical power law but with different critical temperatures. Decomposition of the strain tensor and the squared order parameters to their irreducible representations yields a symmetry-invariant coupling of strain and order parameters in terms of the free energy. Minimizing the free energy at each temperature requires $e_{13} = k_D \cdot Q_D (400 - T)$ and $e_{11} - e_{22} = k_R \cdot Q_R^2 (359 - T)$. Assuming a Landau critical power law $(T_c - T)^{1/2}$ for the order parameters makes the monoclinic angle $\beta \propto (400 - T)^{1/2}$ and the corresponding axial length difference $a - b \propto (359 - T)$. The two relationships are seen in the figure to hold well, close to the critical temperatures. The incompatible symmetry of the E_g mode, leading to the monoclinic distortion, with the A_{1g} mode that originates in the phase transition from cubic to tetragonal and leads to an increasing octahedral $TeBr_6^{2-}$ rotation about $[001]$, results in further rotation becoming blocked by the displacement of the K^+ ions from their special positions and the consequent abrupt change in $c - a$ at 400K. Comparable relationships are expected in all antifluorite structures at the tetragonal-to-monoclinic phase transition, although it is not possible to predict the relative order of the two critical temperatures or their difference by mode analysis. Related structures that are expected to undergo similar soft modes include the elpasolites (e.g. Rb_2NaDyF_6), the cryolites (e.g. $(NH_4)_3FeF_6$) and the $K_3Co(CN)_6$ family; others may include the $K_3Co(NO_2)_6$ family. In each case, careful heat capacity and differential high resolution X-ray diffraction measurement would indicate not only the transition temperatures but would also identify broadened transitions such as that in the accompanying figure at which critical temperature differences become appreciable.



05.1-77 NEUTRON AND X-RAY DIFFUSE SCATTERING AND PHASE TRANSITIONS IN UREA-ALKANE INCLUSION COMPOUNDS. R. FORST, H. JAGODZINSKI, H. BO-VSENER, F. FREY, Institut für Kristallographie der Universität München, Bundesrepublik Deutschland.

The temperature dependence of diffuse scattering in urea inclusion compounds has been investigated by X-ray and neutron diffraction (on MANII at FRM and D10 at ILL, see Act. Cryst. A37 Suppl. 1981, C-112). The understanding was supported by a detailed structure determination of the different phases. Here we concentrate on the various kinds of diffuse intensity, two of which involve phase transitions of the urea host lattice, while the remaining two are due to the guest molecules.

I. At 147K a continuous phase transition from an averaged trigonal to an averaged monoclinic structure (urea with hexadecane) takes place corresponding to a lateral ordering by slight rotations and translational displacements of the nearly rigid urea molecules. At the transition-temperature superstructure reflexions arise - accompanied by twinning - indicating a doubled a, b -component of the unit cell. They are preceded by a critical sharpening and growth of diffuse intensity with decreasing temperature. Within the energy resolution of the instrument D10 only a very small inelastic component was found, i.e. the disorder above 147K is predominantly (quasi) static. Rather low values for the critical exponents have been derived ($\nu = 1.7, \gamma = 3$), possibly indicating a slight first order character.

II. Below 119K the Bragg reflexions are surrounded in c^* -direction by up to ten orders of satellites due to a mutual periodic deformation of guest and host. The appearance of the satellites is preceded by a weak diffuse scattering in c^* -direction. No clear indication of an inelastic part could be found. There is a hysteresis of about 15K around the transition temperature.

III. Continuous layer-lines perpendicular c^* are found in all phases with a period slightly longer than $2c$ of urea. They are sharp along c^* in the whole range and do not change with temperature until 119K, where Bragg-reflexions arise on the layers with h and k of urea. This is explained by screw disorder of the whole chains. No pure translational or rotational disorder is possible as shown by structure analysis. The diffraction pattern at r.t. has been reproduced by calculating Fourier-Bessel-transforms for the chains in their extended planar zig-zag conformation. While X-ray data reveal no difference between a cylinder-symmetrical and a sixfold azimuthal orientation of the chains about their axes, neutron data - making allowance also for the H-atoms - clearly point towards the latter possibility. This is confirmed by the analysis of the contributions of the chains to the $hk0$ reflexions.

IV. Three observable orders of broad (static) diffuse layers (also perpend. c^*) show the typical intensity distribution of a longitudinal disordered 2_1 -helix built by the zig-zag fragments of the alkane chains. The temperature dependence is the same as in section III. The $fwhm$'s do not increase with Q . From them longitudinal displacements of the atoms in the fragments are derived. It is concluded, that the interaction between guest and host takes place by intramolecular distortion of the chains in accordance with the fine structure of the host.

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