THE LOW TEMPERATURE COMMENSURATE PHASE OF SYNTHETIC CO-ÅKERMANITE, $Ca_2CoSi_2O_7$

M. RIESTER , H. BÖHM and V. PETRICEK‡

contact: horst.boehm@.*uni-mainz.de*

Institut für Geowissenschaften, Johannes Gutenberg-Universität, D-55099 Mainz, Germany

‡*Institute of Physics, Academy of Sciences, Prague, Scech Republic*

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Background of the investigations

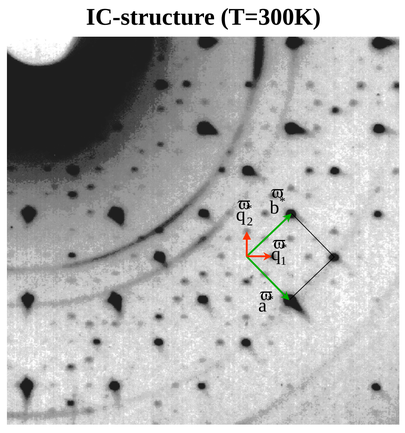
Co-åkermanite ($Ca_2CoSi_2O_7$) exhibits a two-dimensional incommensurate modulation at roomtemperature. A structure model for the roomtemperature IC-phase was determined using the superspace approach by Hagiya et al (1993). The symmetry is described by the (3+2)-dimensional superspace group [(pp0, -pp0) $P42_1m$ / P4mg], with wavevectors $q_1 = \alpha\,(a^*+b^*)$, $q_2 = \alpha\,(-a^*+b^*)$ with $\alpha = 0.2913$.

The modulation of åkermanite type layer compounds can be controlled by cationic substitution and temperature variation. The phase transition between the incommensurate phase and the parent phase is known for various åkermanit compounds. This high temperature phase transition is of second order. A low temperature phase transition to a commensurate lock-in structure was predicted.

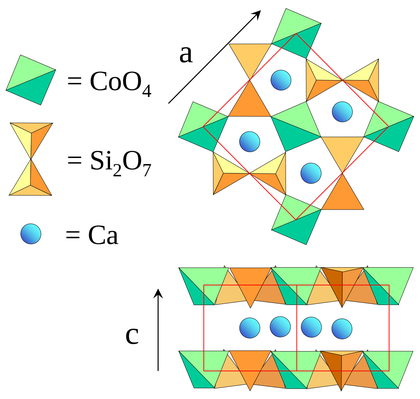
We present investigations of the lock-in phase transition and the lock-in structure of $Ca_2CoSi_2O_7$.

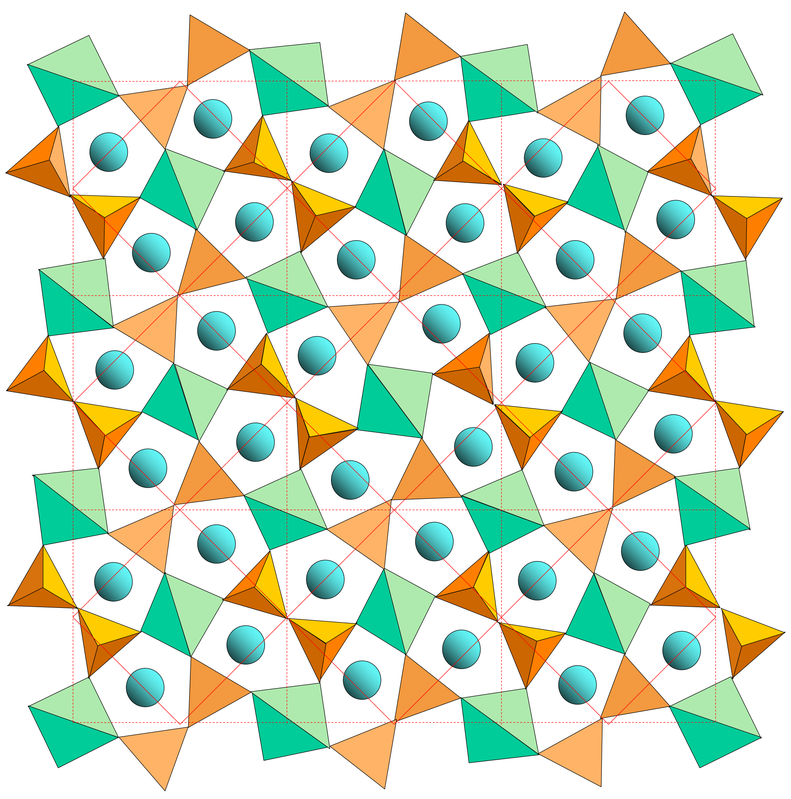
Plane (h k 0) of the reciprocal lattice

IC-structure (T=300K)



Basic åkermanite structure





Lock-in structure at T = 130K

Model:

(3×3×1) supercell

$\overline{S}G$: P4; twinned (m_{xy}) model group for SiO_4 element specific isotropic temperature parameters

R-values:

$R_{obs(all)}$ = 0.092

$R_{obs(main)}$ = 0.046

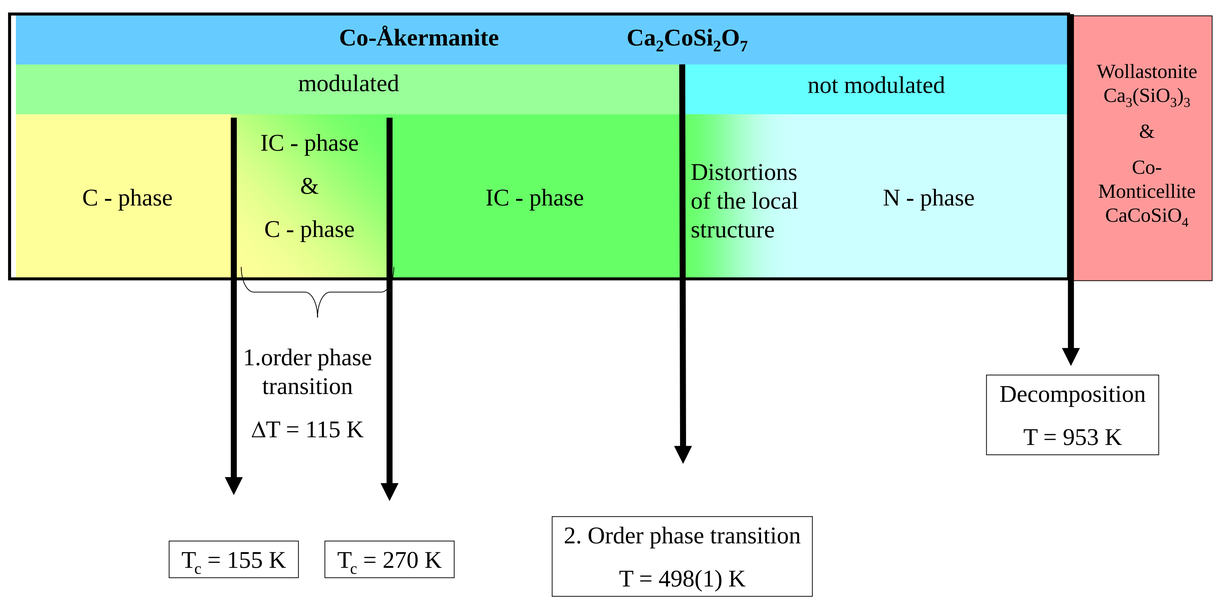
$R_{obs(satellites)}$ = 0.142

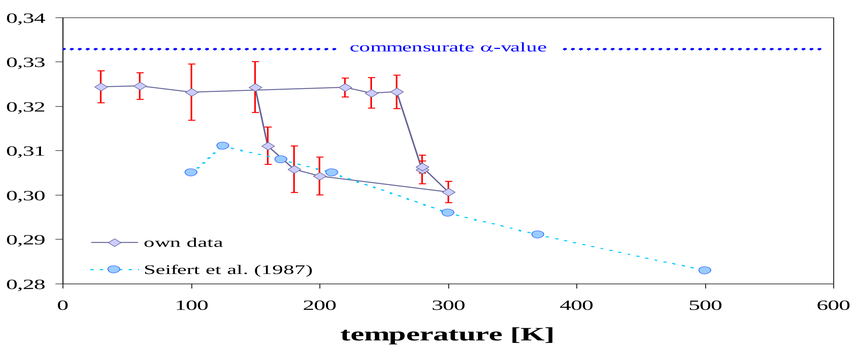
Structural features:

Coordination < [8] for $^2/_3$ of the calcium atoms

Maximum bending angle of Si_2O_7 group is 28°

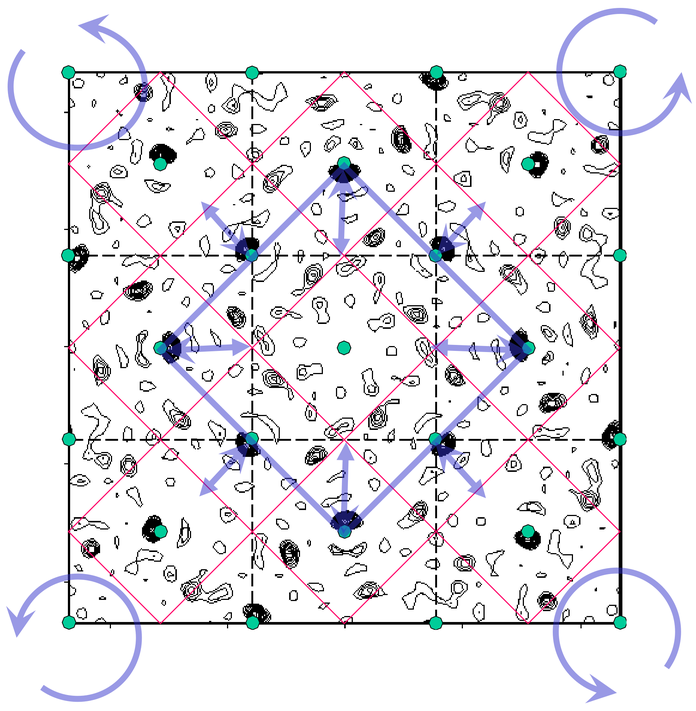
Temperature dependent phase sequence for quenched Co-Åkermanite at P = 1 bar





α(T) shows the lock-in phase transition between the IC- and the C- structure. The prominent hysteresis indicates the stability of the lock-in structure.

The magnitude of the error bars is 1σ



Distortion modes of the tetrahedral layer

The partial fourier synthesis of the satellites for z = 0 reveals the distortion of the tetrahedral layer in the lock-in structure with respect to the unmodulated structure. The displacements of the cobalt atoms in one individual of the twinned structure follow an in-phase rotational mode around (0,0,0) and an anti-phase breathing mode around ($^1/_2$,$^1/_2$,0). The rotational modes of the two indviduals are anti-phase, whereas the breathing modes are in-phase.

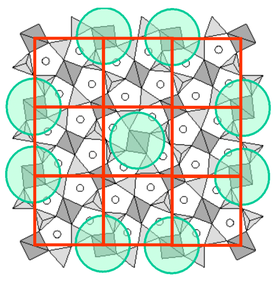
Local distortion patterns of the modulated phases:

Distinct local distortion patterns are observed for the incommensurate- and the lock-in- structure. These distortion patterns describe the arrangement of strongly distorted structural units. These units are characterized by an enlarged CoO_4 tetrahedron surrounded by strongly bent Si_2O_7 groups and calcium in [6]- and/or [7]-fold coordination.

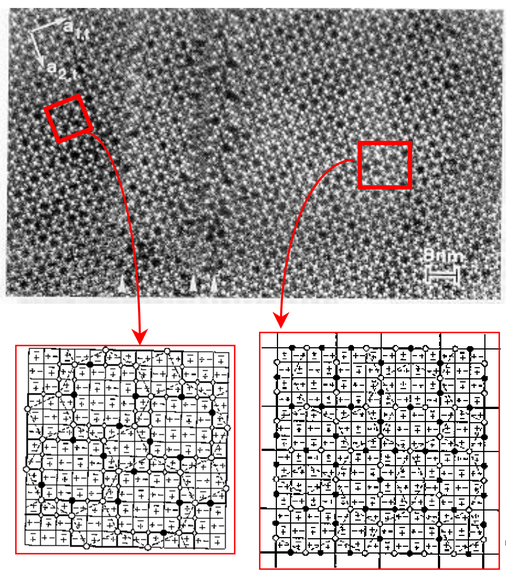
TEM investigations of $Ca_2ZnGe_2O_7$ by Van Heurck et al. (1990) show an octagonal arrangment (Ø = 4 unit cells) of these structural units in the IC-structure. The long range ordering of this octagonal distortion pattern is temperature dependent. The structure model for the IC-structure of $Ca_2CoSi_2O_7$ by Hagiya et al. (1993) leads to the same local distortion pattern.

In the lock in structure these units form a centred octagonal arrangement (Ø = 3 unit cells). The long range ordering of this distortion pattern is most likely not temperature dependent.

The ratio of ($Ca^{[8]}$: $Ca^{<[8]}$) decreases from the N-phase (1:0) over the IC-phase (≈ 7:2) to the lock-in phase (1:2). The structural distortions responsible for the modulation lead to the generation of low coordinated calcium sites.



The green circles mark the structural units with low coordinated calcium. Comparing the long range ordering patterns of these topologies in the two modulated phases, the denser arrangement is observed in the lock-in structure (left figure).



TEM investigation of $Ca_2ZnGe_2O_7$ by Van Heurck et al (1990) (above). The authors describe an octagonal distortion pattern. The only qualitative description of the structure distortions leads to a microdomain model characterized by sharp antiphase boundaries. A quantitative evaluation of the structure distortions is possible from the structure determination of $Ca_2CoSi_2O_7$ by Hagiya et al. 1993 (below).