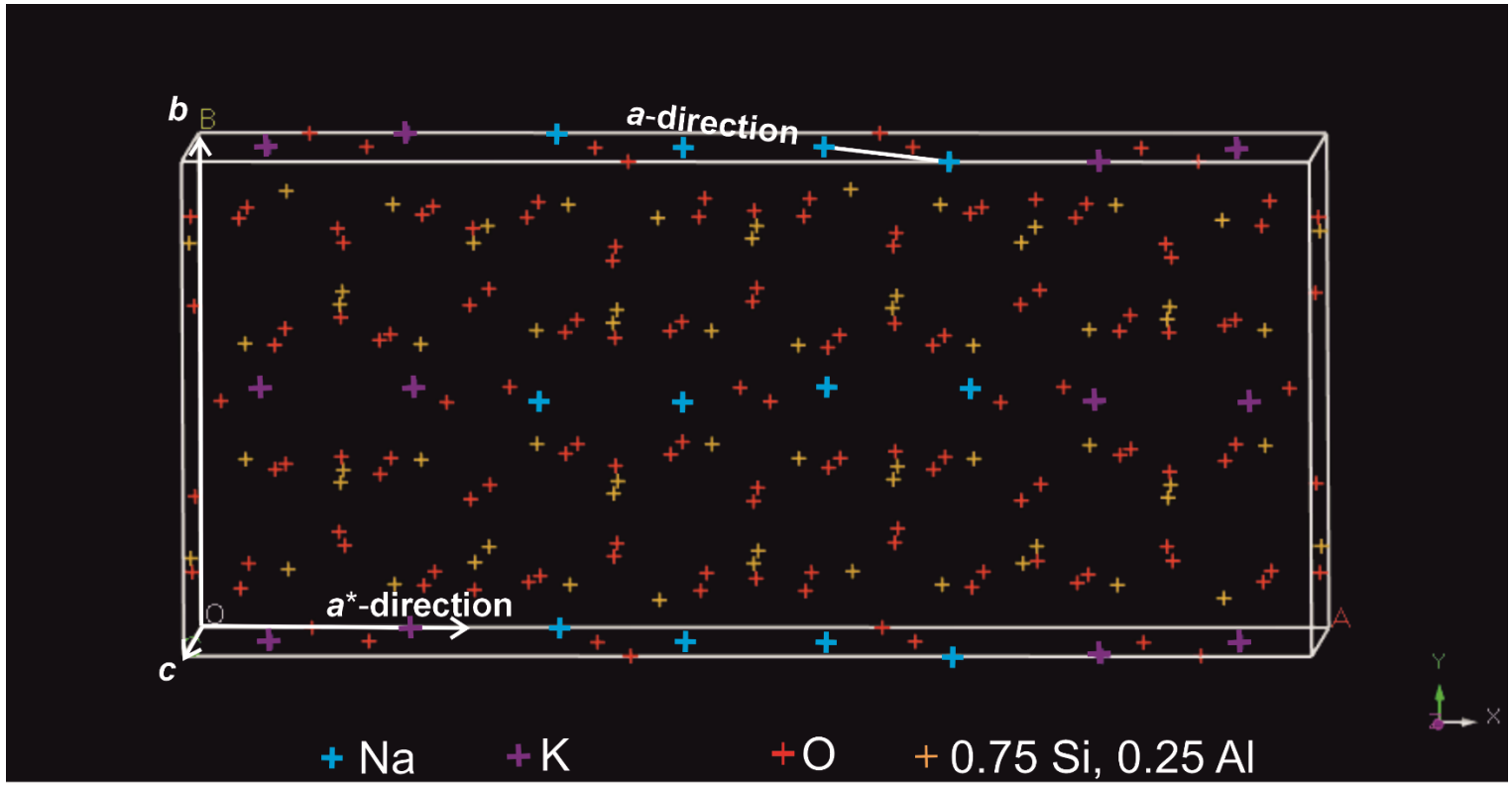
Supplementary

from the study “Coherent lamellar phase decomposition of alkali feldspar studied by a microscopic approach” published by Artur Benisek, Edgar Dachs, Gregor Zickler, Rainer Abart in Phys Chem Minerals:

Supplementary A: Structural models

Fig. A1 Monoclinic (P2/m) alkali feldspar structure with coherently decomposed phases.

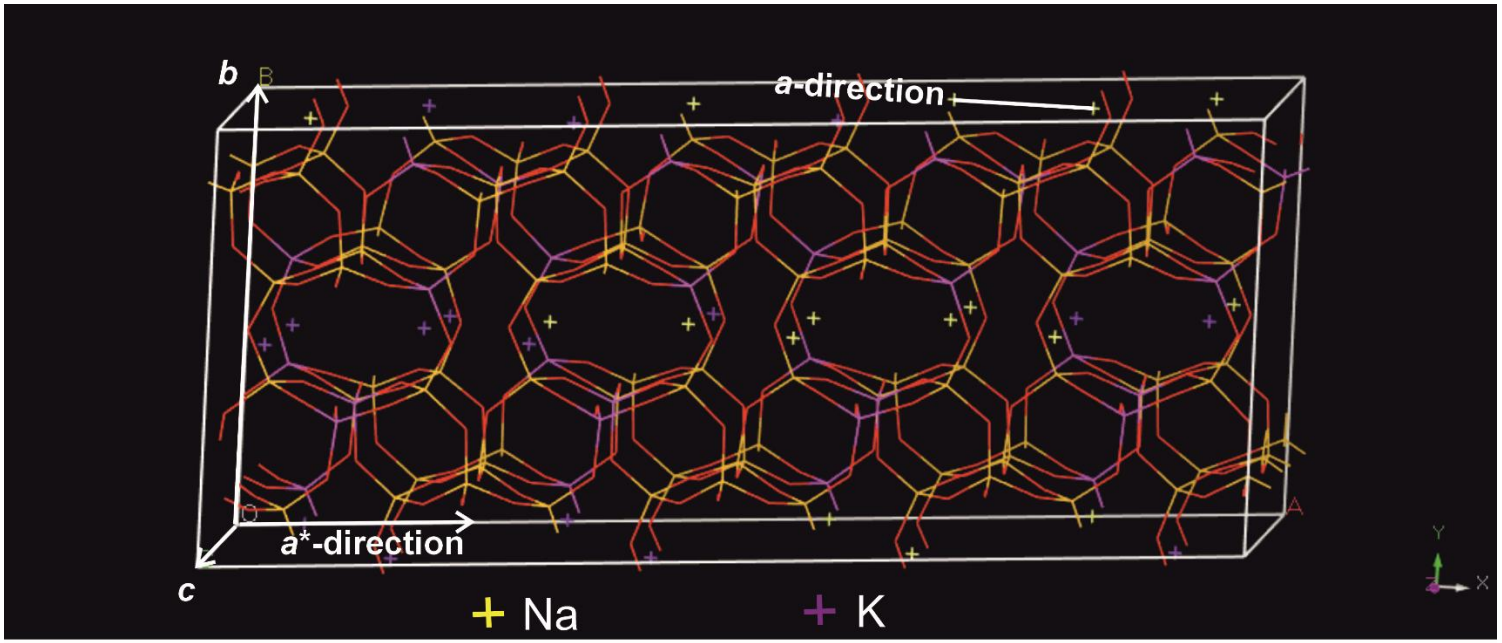
The lamellae thickness d = 2 a_0, the chemical gradient ∇ = 2.



K-content	100	100	0	0	0	0	100	100

Fig. A2 Triclinic alkali feldspar structure (P1-symmetry) with coherently decomposed phases.

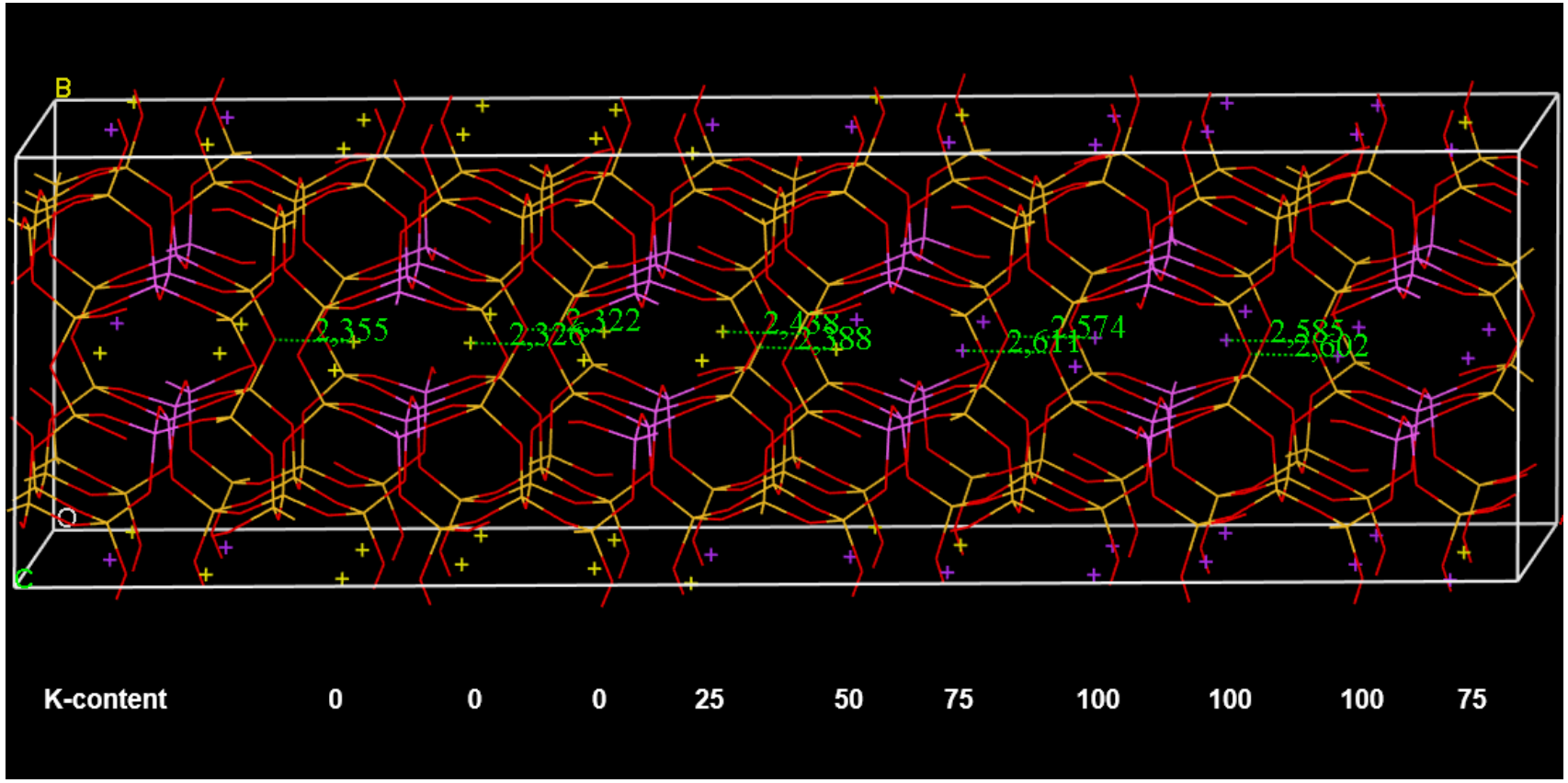
The lamellae thickness $d = 2\ a_0$, the chemical gradient $\nabla = 0.5$.



The interface is perpendicular to the a*-direction and parallel to the b, c-plane. The Na and K atoms forms also planes that are parallel to the interface. The composition of each such Na, K-plane is given by the numbers (K-content) below the figures.

To investigate the Na, K-bond lengths relaxation away from the interface, two structures were used. One is the structure shown in Fig. A1 with Al and Si mixing on site (0.25 Al and 0.75 Si on each tetrahedral site). The other structure is shown below (Fig. A3), which is characterised by a regular Al/Si configuration pattern to guarantee that every Na, K-O polyhedra in a chain that is oriented perpendicular to the interface have the same tetrahedral environment.

Fig. A3 Cell with regular Al/Si configuration pattern (consistent with PM symmetry). The lamellae thickness d = 3 a_0, the chemical gradient ∇ = 0.5. The Na, K-chain for investigating the Na, K-O bond lengths relaxation (see Fig.2) is highlighted by the Na, K-O_{A2} bonds. Another chain has a different atomic environment. Using Na, K-O polyhedra from different chains deliver thus meaningless results. Symbols as shown in Fig. A2.



Examples for the compositions at the interface

K-content (at. %) of each Na, K-planes that are parallel to the interface

Below, three examples are presented how the interface was modelled. The lines list the composition of the Na, K-planes that are parallel to the interface. The first line represents a cell, where the two lamellae are separated by a sudden change in composition. The gradient in this example is $\nabla = 2$. The second line show an example, where the two lamellae have a transitional step between them generating $\nabla = 1$. The third example show a smooth transition where the composition is changed in four steps ($\nabla = 0.5$).

K-content (at. %) of Na, K-planes								**Chemical gradient**	
100	**100**	**100**	**100**	**0**	**0**	**0**	**0**	$\nabla = \frac{\Delta X}{a_0} = \frac{1}{0.5} = 2$	see Fig. A1
100	**100**	**100**	**50**	**0**	**0**	**0**	**50**	$\nabla = \frac{1}{1} = 1$	
75	**100**	**75**	**50**	**25**	**0**	**25**	**50**	$\nabla = \frac{1}{2} = 0.5$	see Fig. A2

There are two Na, K-planes parallel to (100) per a_0 lattice parameter.

Supplementary B: TEM investigations

on coherently decomposed samples used for calorimetric work:

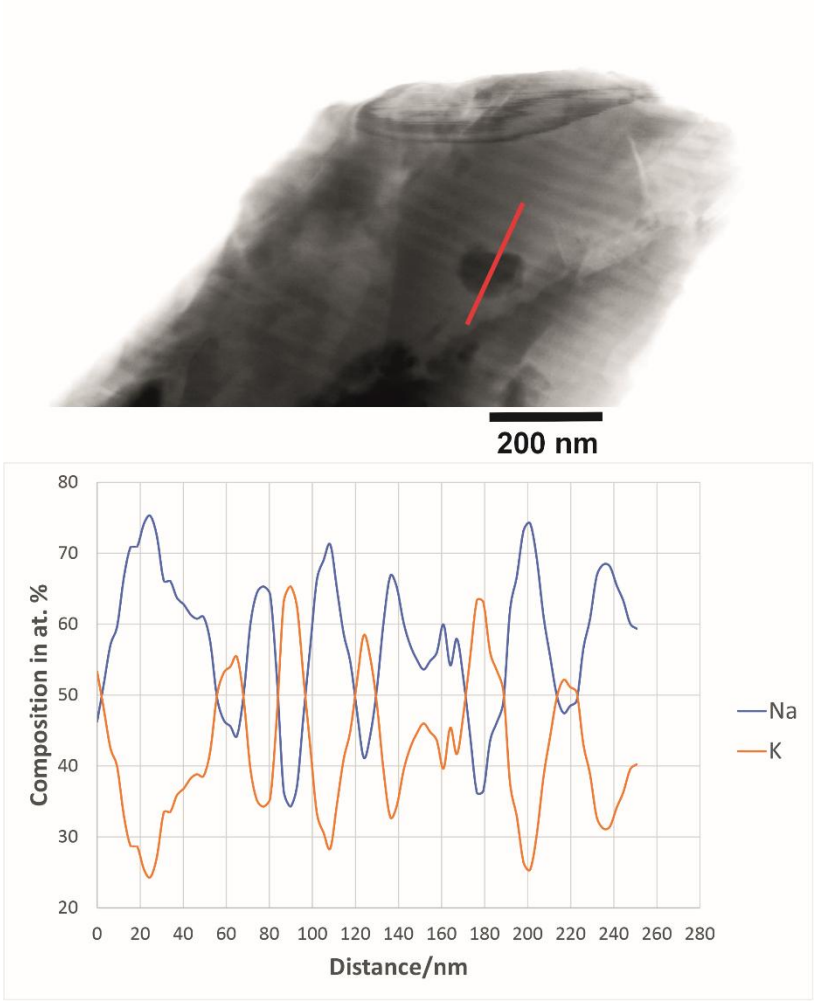


Fig. B1: STEM bright field image of the chemical variation along *a*-direction. The K-rich lamellae have a lower intensity and therefore appear darker as the Na-rich lamellae in the STEM bright field image, due to the higher atomic number of the potassium atoms.

The mean lamellar thickness is ~ 20 nm and corresponds to a thickness of ~ 24 a_0 lattice constants. The compositions of the Na- and K-rich lamellae are ca. $Na_{75}K_{25}$ and $Na_{40}K_{60}$, respectively.

The accuracy of the TEM data may be judged by calculating the mean composition from all values resulting in $Na_{58}K_{42}$, which is exactly the composition of the homogenous sample.

Supplementary C: Coherency strain energy results

Table C1: Coherency strain energies of investigated samples. ΔH^{CS} and k^h are related by $\Delta H^{CS} = k^h (X_K - X_K^0)^2$.

Exp. Nr.	Crystal Structure	Gradient ∇ in $\Delta X_K/a_0$	Lamellae-thickness d in a_0	Degree of decomposition $X_K - X_K^0$	Coherency strain energy ΔH^{CS} in kJ/mol	Coherency strain energy coefficient k^h in kJ/mol	Origin
1	P1	0.5	2	0.5	0.702	2.81	DFT
2	C2/m	0.47	13	0.22		2.34	Heuser et al. 2024
3	C2/m	0.47	15	0.18		1.79	Heuser et al. 2024
4	C2/m	0.47	26	0.07		1.63	Heuser et al. 2024
5	P1	1	1	0.25	0.466	7.46	DFT
6	P1	1	2	0.25	0.395	6.32	DFT
7	P1	1	3	0.25	0.370	5.92	DFT
8a	P1	1	4	0.5	1.36	5.20*	DFT
8b	PM	1	4	0.5	1.24		
9	P2/m	2	2	0.5	2.54	10.2	DFT
10	P1	2	2	0.5	3.08	12.3	DFT

* Mean value from experiment 8a and 8b, differing in crystal structure.

Supplementary D: Strain energy coefficient for the vibrational entropy (k^S)

plotted as a function of the chemical gradient (∇):

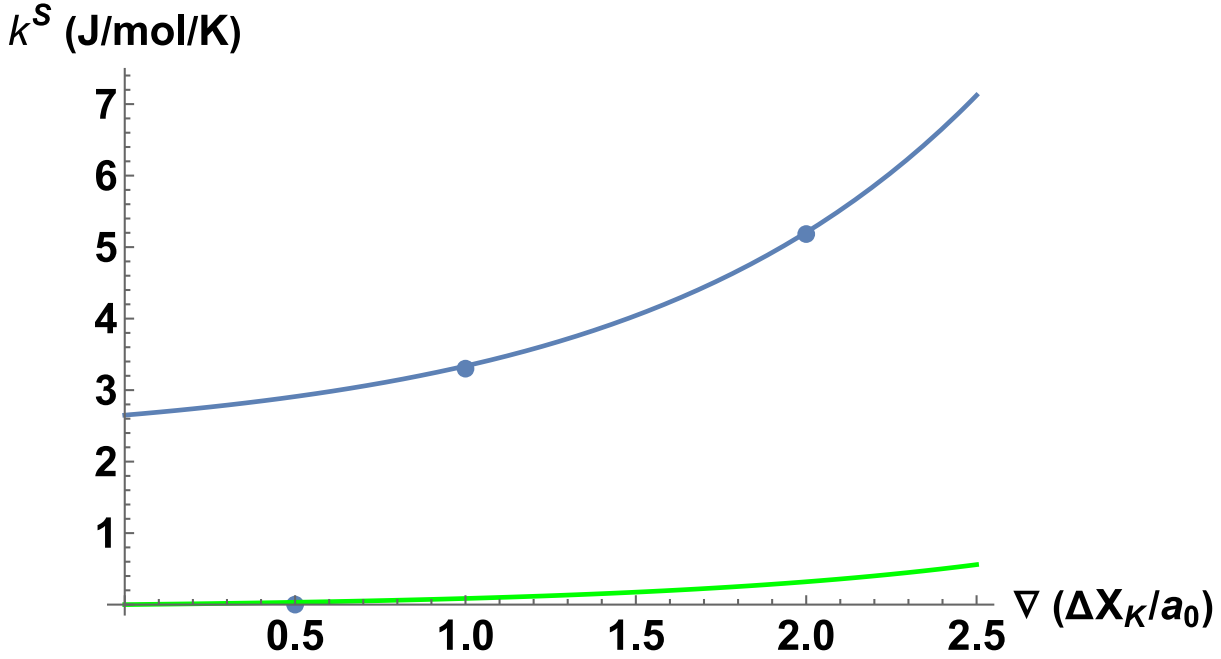


Fig. D1: The upper curve (defined by the two DFT values) corresponds to samples with a lamellae thickness of d = 1 a_0, the lower with d = 24 a_0. This curve is defined by a calorimetric value. The coherency strain in alkali feldspars is not able to generate negative excess vibrational entropies as worked out in chapter 3.2. Since the calorimetric determined value is zero, the lower curve is defined well with only one point, at least for a chemical gradient of $\nabla < 1\ \Delta X_K/a_0$, which in turn is the relevant region. For determining k^S versus ∇ relations with lamellae thicknesses between 24 and 1 a_0, an exponential interpolation function was used.

Supplementary E: Correction of the degree of decomposition

The composition profile along the *a**-axis may be simplified by a trapezoid:

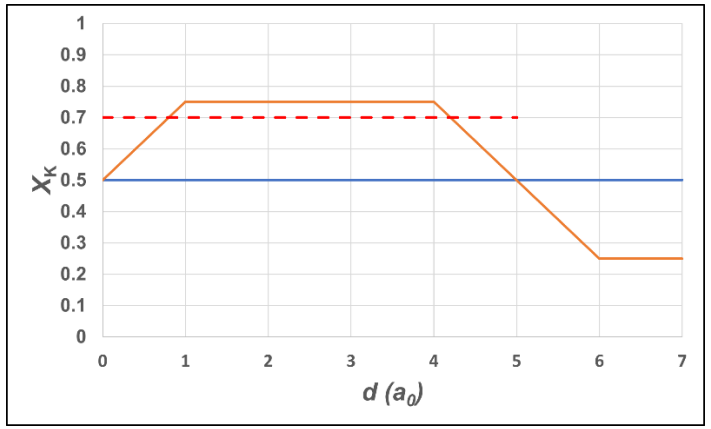


Fig. E1 Compositional variation along the *a**-axis

d = 5 a_0
$(X_K - X_K^0)^{max}$ = 0.25
X_K^0 = 0.5
∇ = 0.25 $\Delta X_K/a_0$

From geometric considerations, a correction factor (*corr*) can be defined that relates the mean decomposition, $(X_K - X_K^0)^{mean}$, to the maximal decomposition, $(X_K - X_K^0)^{max}$, depending on the chemical gradient (∇), the lamellae thickness (d), and the maximal decomposition $(X_K - X_K^0)^{max}$:

$$corr = 1 - \frac{(X_K - X_K^0)^{max}}{d \cdot \nabla}$$

The maximal decomposition is reduced by this correction factor to obtain the mean decomposition, i.e.,

$$(X_K - X_K^0)^{mean} = (X_K - X_K^0)^{max} \cdot corr.$$

The enthalpy and entropy of mixing, ΔH^{mix} and ΔS^{mix}, must be calculated based on this mean decomposition.

Example from Fig. E1:

$d = 5\ a_0$

$(X_K - X_K^0)^{max} = 0.25$

$\nabla = 0.25\ \Delta X_K / a_0$

$\rightarrow corr = 0.8$

Mean decomposition:

$(X_K - X_K^0)^{mean} = 0.25 \cdot 0.8 = 0.2$

(broken red line in Fig. E1)

Check: looking to Fig. E1, it becomes evident:

3 a_0 with $X_K - X_K^0 = 0.25$ and 2 a_0 with 0.25/2 $\rightarrow$ $(X_K - X_K^0)^{mean} = \frac{4 \times 0.25}{5} = 0.2$