SUPPORTING INFORMATION

Spatially-ordered Nano-Sized Crystallites formed by Dehydration-Induced Single Crystal Cracking of CuCl$_2$·2(H$_2$O)

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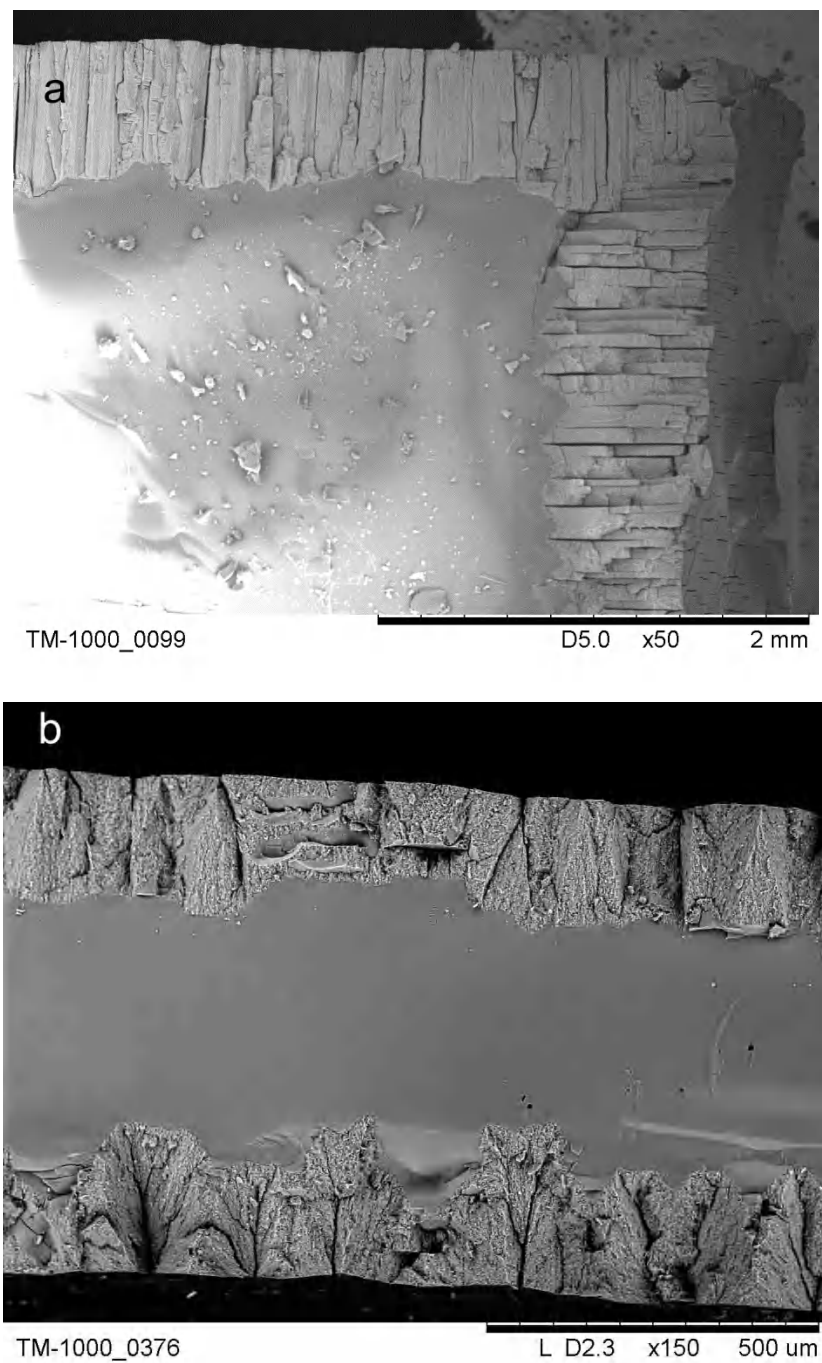[2]*Novosibirsk State University, ul. Pirogova, 2, Novosibirsk 630090 Russian Federation*
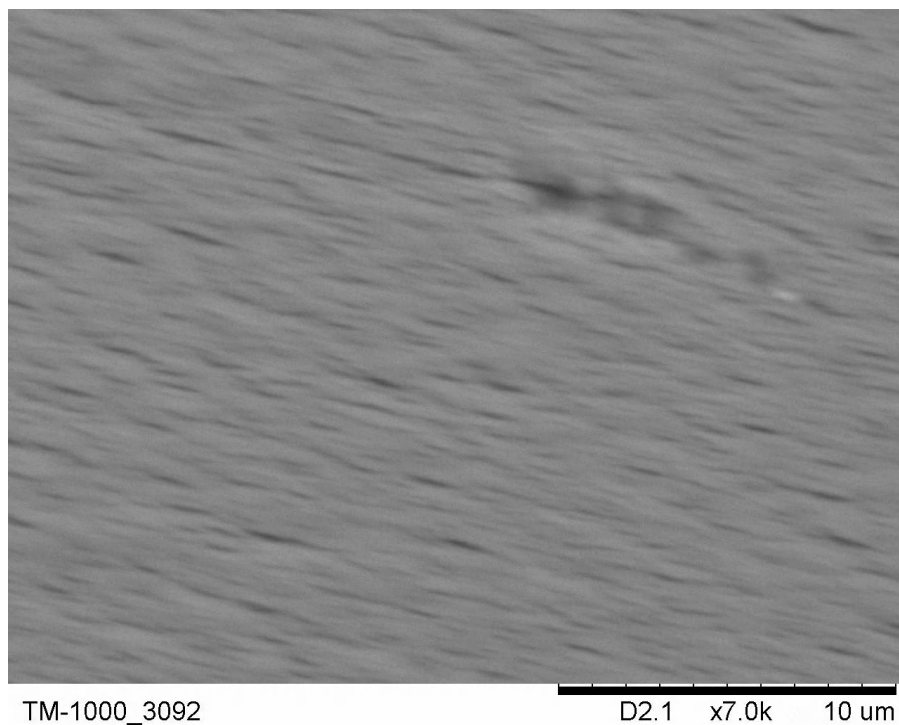
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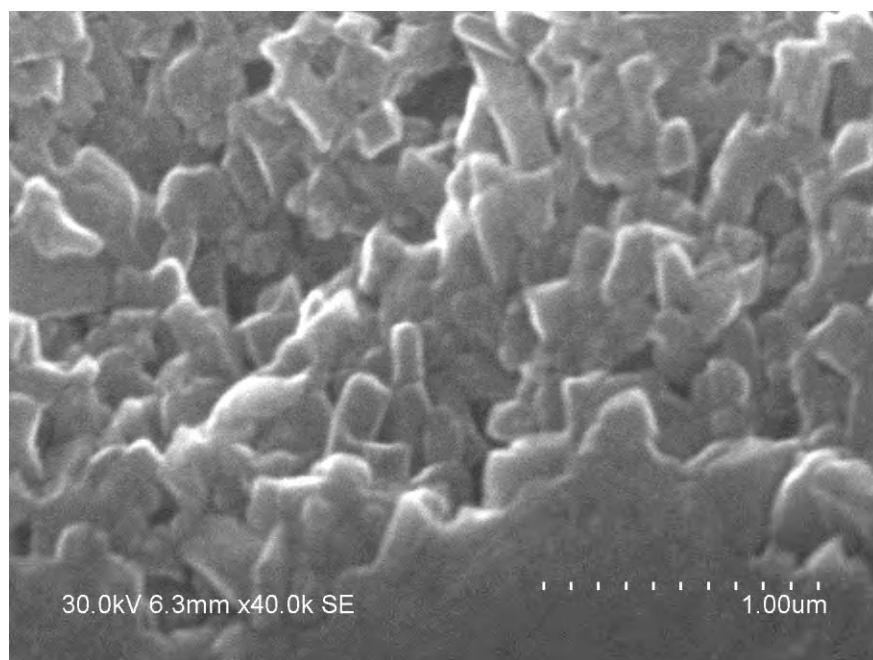
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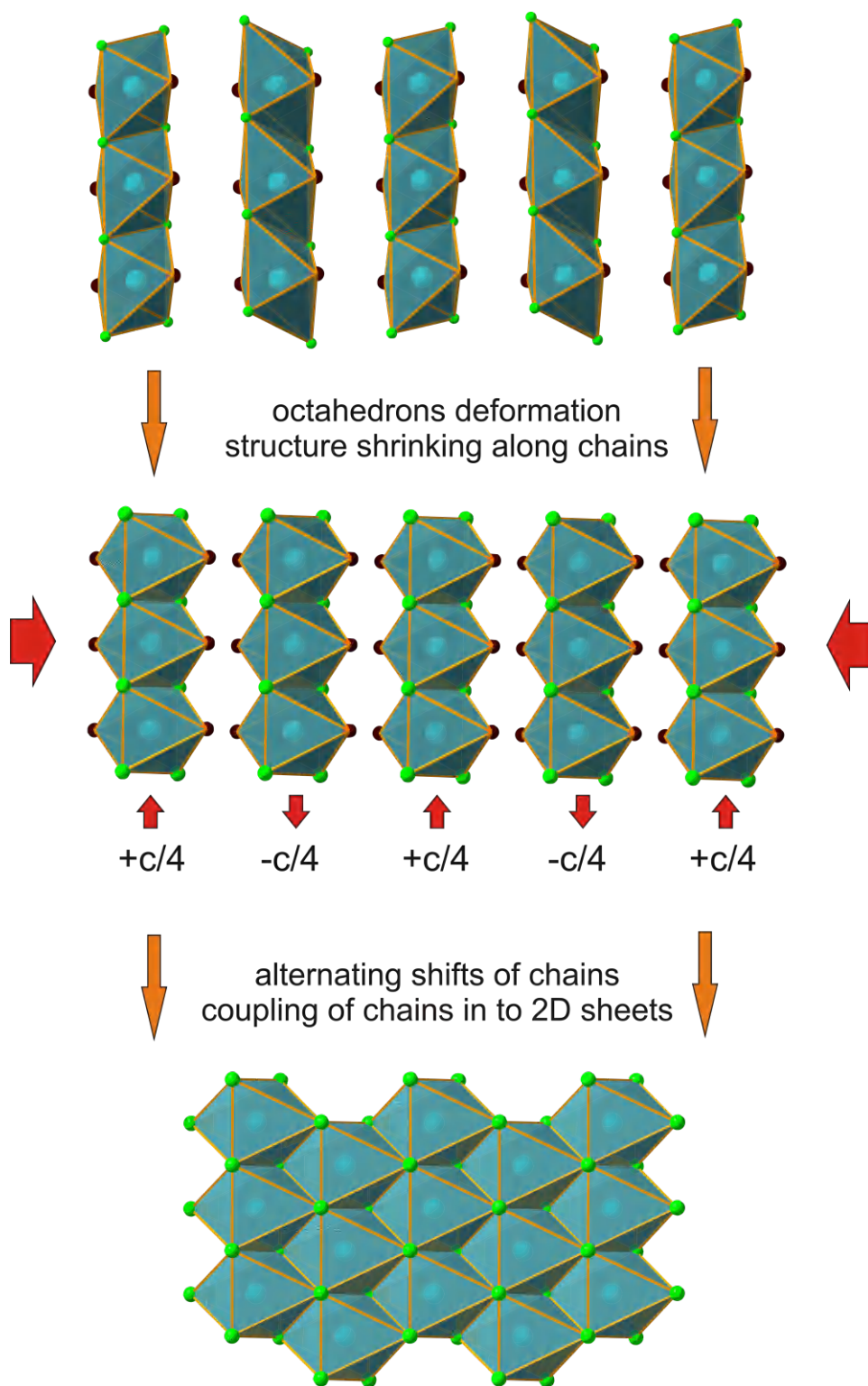
Figure S4. Schematic structure transformation showing coupling of $[CuCl_4(H_2O)_2]$ chains lying in (110) plane of the initial hydrate into 2D $CuCl_2$ sheets lying in (001) plane of the final anhydrous product. Positions of water are shaded in the initial structure.

Calculation of the transformation strain tensor

In case of uniform deformation of a volume, any vector r_0 from the initial volume transforms to a corresponding vector r_1 in the deformed volume according to relation

$$r_1 = \mathbf{F}r_0 \tag{S1}$$

where $\mathbf{F}$ is known as the deformation gradient tensor. By combining three non-coplanar vectors from the initial volume into a matrix $\mathbf{R}_0$ (vectors as columns) we can write

$$\mathbf{R}_1 = \mathbf{F}\mathbf{R}_0 \tag{S2}$$

which gives a corresponding matrix $\mathbf{R_1}$ of three non-coplanar vectors from the deformed volume. Due to selection of non-coplanar vectors, it can be determined that

$$\mathbf{F} = \mathbf{R}_1\mathbf{R}_0^{-1}. \tag{S3}$$

The corresponding Green-Lagrangian strain tensor ε is by definition

$$\varepsilon = \frac{1}{2}\left(\mathbf{F}^T\mathbf{F} - \mathbf{E}\right) \tag{S4}$$

where $\mathbf{E}$ is the identity tensor. The deformation necessary to transform $CuCl_2$ lattice into $CuCl_2\cdot2(H_2O)$ lattice can be determined from this by defining $\mathbf{R_1}$ (for hydrate) and $\mathbf{R_0}$ (for anhydrous phase in orientation I) according to cells' basis vectors and structure relationships given by Table 1.

$$\mathbf{R}_0 = \begin{pmatrix} 6.833 & 0 & 6.567\cos(119.794) \\ 0 & 3.433 & 0 \\ 0 & 0 & 6.567\sin(119.794) \end{pmatrix}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$$

$$\mathbf{R}_1 = \begin{pmatrix} 7.4141 & 0 & 0 \\ 0 & 8.0886 & 0 \\ 0 & 0 & 3.7458 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{S5}$$

This gives following strain tensor for orientation I (in coordinates of the hydrate structure)

$$\varepsilon^I = \begin{pmatrix} 0.789 & 0 & 0.032 \\ 0 & 0.095 & 0 \\ 0.032 & 0 & -0.039 \end{pmatrix} \tag{S6}$$

Further calculation of eigenvalues and eigenvectors of this tensor allows obtaining the diagonalized form of the strain tensor (Eq (8) in the main text) and orientation of principal axes corresponding to the orientation I (given in the text as angles between corresponding axes). Orientations of principal axes for the product phase orientation II can be obtained by applying corresponding mirror symmetry operation to the system for orientation I.

Similar calculations for orientations III and IV give slightly different principal strains

$$\varepsilon^{III} = \begin{pmatrix} 0.802 & 0 & 0 \\ 0 & 0.095 & 0 \\ 0 & 0 & -0.045 \end{pmatrix} \tag{S7}$$

Axes ($\mathbf{X}$, $\mathbf{Y}$, $\mathbf{Z}$) of the corresponding principal systems for III are oriented as following: $\mathbf{Y} \| c$ of the initial structure, angle between $\mathbf{X}$ and a axis of CuCl$_2$: $(\mathbf{X}, a) = 6.96$, angle between $\mathbf{X}$ and b axis of the hydrate structure $(\mathbf{X}, b) = 38.38$. Principal system for orientation IV is obtained by the mirror symmetry operation between III and IV.

Determination of the stressed state of I+II composition in the region of main crack tip

To estimate the elastic energy density for the region near main crack tip we can assume formation of 1:1 composition of two orientations (I and II) in this region. The apparent elasticity tensor of the composition can be estimated following an approach similar to Hill's method of averaging elastic moduli of polycrystalline material[S1]

$$C^{comp} = \frac{1}{2}\left(\frac{C^I + C^{II}}{2} + \left(\frac{S^I + S^{II}}{2} \right)^{-1} \right) \tag{S8}$$

where C's and S's are 6x6 Voight matrix notations of corresponding elasticity and compliance tensors ($S=C^{-1}$). By applying the rotation transforms to the matrices $C^{I/II}$ and $S^{I/II}$ (whose coefficients are defined by Table 3 in the main text) required for the transition to the local Cartesian system of the main crack tip (local Cartesian axes $\mathbf{1}$, $\mathbf{2}$ and $\mathbf{3}$ are parallel to a, c and b axes of the initial structure) we obtain the stiffness matrix of an effectively orthorhombic material

$$C^{\text{comp}} = \begin{pmatrix} 25.8 & 14.3 & 15.4 & 0 & 0 & 0 \\ 14.3 & 43.2 & 15 & 0 & 0 & 0 \\ 15.4 & 15 & 27 & 0 & 0 & 0 \\ 0 & 0 & 0 & 8.6 & 0 & 0 \\ 0 & 0 & 0 & 0 & 12 & 0 \\ 0 & 0 & 0 & 0 & 0 & 8.3 \end{pmatrix} \text{GPa} \tag{S9}$$

An apparent strain tensor of the composition can be estimated from average deformation gradient tensor

$$\mathbf{F}^{\text{comp}} = \frac{1}{2}\left(\mathbf{F}^{\text{I}} + \mathbf{F}^{\text{II}}\right) \tag{S10}$$

where $\mathbf{F}^{\text{I/II}}$ are deformation gradient tensors for orientations I and II transformed by rotation operations from the principal systems of I and II to the local Cartesian system of the main crack tip. By performing these calculations one can obtain

$$\varepsilon^{\text{comp}} = \frac{1}{2}\left(\left(\mathbf{F}^{\text{comp}}\right)^T \mathbf{F}^{\text{comp}} - \mathbf{E}\right) = \begin{pmatrix} 0.268 & 0 & 0 \\ 0 & 0.095 & 0 \\ 0 & 0 & 0.379 \end{pmatrix} \tag{S11}$$

References

S1. R. Hill, *Proceedings of the Physical Society. Section A* 1952, **65** (5), 349