Stress anisotropy severely affects zinc-phosphate network formation

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This supplementary information contains the radial distribution functions (RDF) $g(r)$ of the system and it's development with the deformation for the three deformation shapes discussed in the main text. We included a brief comparison of the obtained results with data on $\alpha{-}\mathrm{Zn}_2(\mathrm{PO}_4)_3$ in Sec. II. In the last part of this document, namely in Sec. III, we provide analytical formulas for components C_{ii} $(i = 1, 2, 3)$ of elastic tensor in the rotated coordinate system.

I. RADIAL DISTRIBUTION FUNCTION

In all three runs, as the pressure or strain is increased, we observe similar two-body correlation functions. The changes are continuous, and the difference between $g(r)$ functions for two nearest deformation values is extremely small. However, at a pressure of 5 GPa we observe slight changes in $g_{\mathrm{Zn-O}}(r)$ in the case of isotropic compression, which is depicted in Fig. S1(a). For uniaxial and density-conserving deformations the critical strain values are $\varepsilon = -0.24$ (Fig. S2(a)) and $\varepsilon = 0.30$ (Fig. S3(a)), respectively. The changes seem to be very subtle or elusive: the peak position of Zn-O RDF shifts to slightly larger distances, and the magnitude of the peak becomes slightly higher. In order to quantify the changes, we applied the skewed-normal distribution analysis [1] (SND) to the calculated functions. Examples of the fit of the first peak of the function $\mathrm{Pr}(r) = 4\pi r^2 \rho g(r)$ are shown in the insets of Fig. S1(a), Fig. S2(a) and Fig. S3(a). As a result of such analysis, we noticed, that the average coordination number of Zn atoms changes (quasi-) discontinuously at the critical pressure of $p_\mathrm{c} = 5$ GPa from a value close to 4 to a value close to 4.5 for isotropic compression. Similar conclusions were obtained for both uniaxial deformations as well. The respective changes in the coordination number of zincs are depicted in Fig. S1(b) for isotropic, in Fig. S2(b) for uniaxial and in Fig. S3(b) for density-conserving compressions. This means, that the local environment of Zn atoms changes abruptly at the transition.

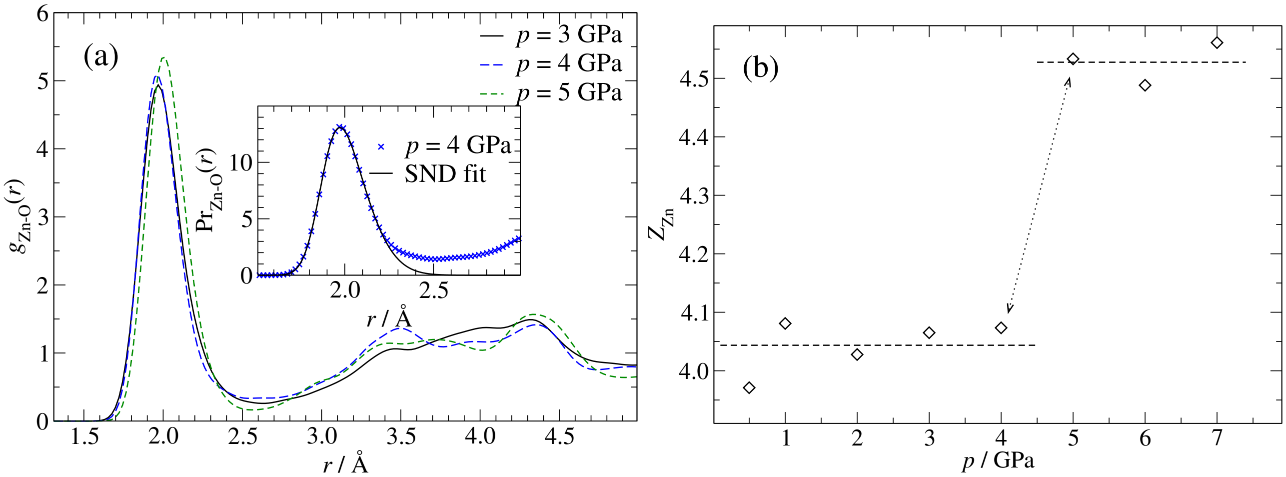

FIG. S1. Evolution of (a) radial distribution function $g_{\mathrm{ZnO}}(r)$ as a function of pressure, and dependence of (b) coordination number Z of Zn atoms deduced from $g_{\mathrm{ZnO}}(r)$ on pressure in the isotropic compression run. The inset of subfigure (a) shows the example of an skewed normal distribution (SND) fit of the probability distribution function $\mathrm{Pr}_{\mathrm{ZnO}}(r)$, from which Z_{Zn} is deduced.

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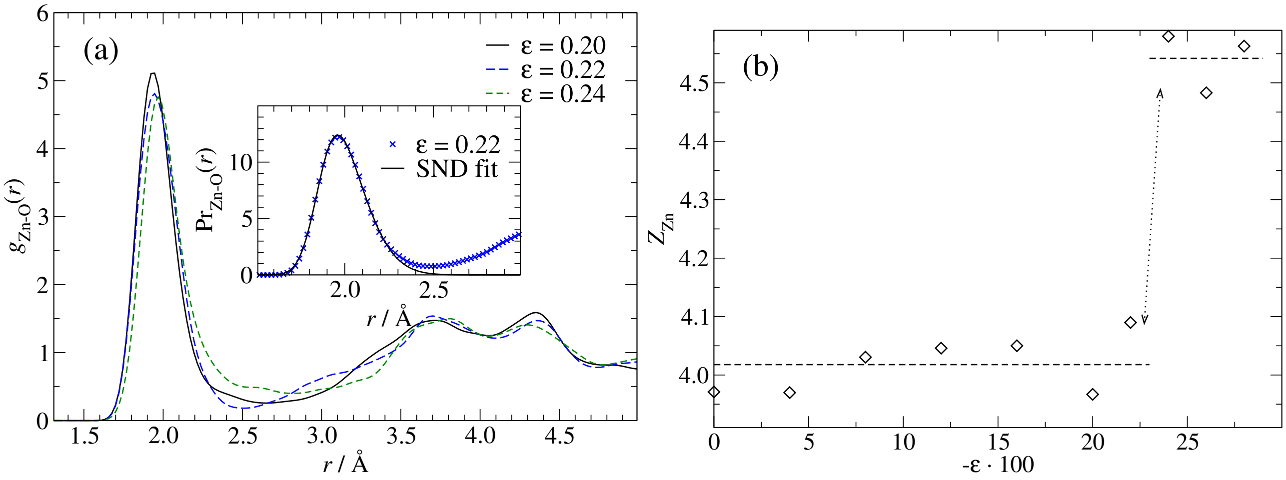

FIG. S2. Evolution of (a) radial distribution function $g_{\mathrm{ZnO}}(r)$ as a function of strain ε, and dependence of (b) coordination number Z of Zn atoms deduced from $g_{\mathrm{ZnO}}(r)$ on strain in the uniaxial deformation run. The inset of subfigure (a) shows the example of an SND fit of the probability distribution function $\mathrm{Pr}_{\mathrm{ZnO}}(r)$, from which Z_{Zn} is deduced.

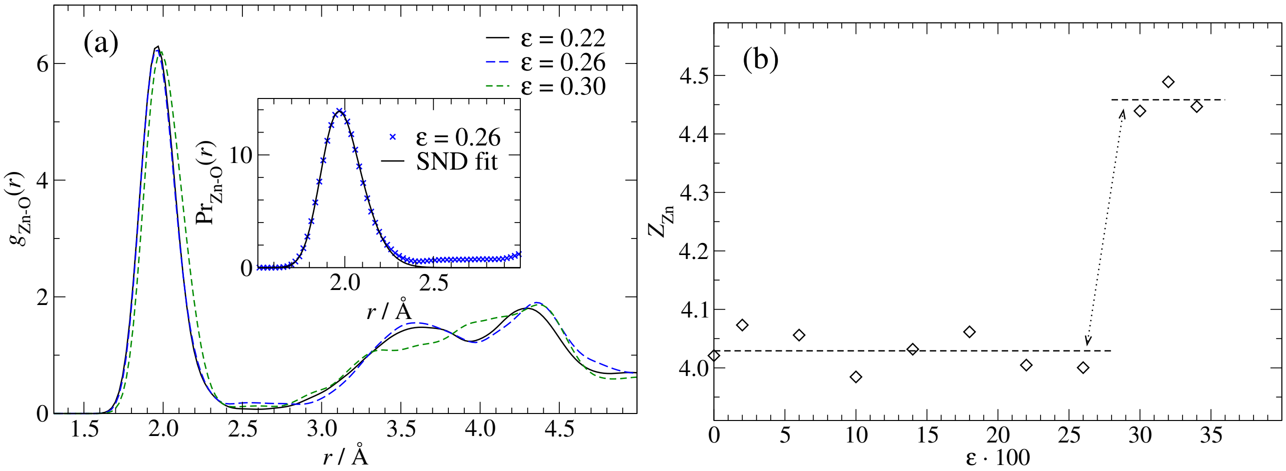

FIG. S3. Evolution of (a) radial distribution function $g_{\mathrm{ZnO}}(r)$ as a function of strain ε, and dependence of (b) coordination number Z of Zn atoms deduced from $g_{\mathrm{ZnO}}(r)$ on strain in the density-conserving deformation run. The inset of subfigure (a) shows the example of an SND fit of the probability distribution function $\mathrm{Pr}_{\mathrm{ZnO}}(r)$, from which Z_{Zn} is deduced.

II. ORTHOPHOSPHATE

To make a connection between zinc phosphates considered in this study and described in the main text, with a crystalline system similar in composition, which would be subjected to undergo a phase transformation similar to the observed in this work, we chose to apply the same deformations to the α-$\mathrm{Zn}_2(\mathrm{PO}_4)_3$. It is relatively well understood what happens with this crystal under isotropic compression. In a few experimental studies the authors observed pressure-induced amorphization of zinc orthophosphate which was accompanied by a change in the coordinate number of Zn atoms [2, 3]. However, the question remains open on how shear affects α-$\mathrm{Zn}_2(\mathrm{PO}_4)_3$.

In attempt to shed some light on this, we conduct a set of static calculations at zero temperature. At first, we applied a static compression at a fixed external pressure. When pressure reached $p = 9$ GPa, the crystal underwent local structure changes, where one third of Zn atoms adopted seesaw local geometry, and the rest of zincs got coordination changed from four to five with local structure which could be considered to be a slightly deformed trigonal bipyramid, thus getting closer to being square pyramidal. This value of critical pressure is in a good agreement with a previously reported result of 9 GPa [2]. Then we proceeded with the anisotropic deformations, which included a uniaxial compression along z-axis, and the same volume-conserving deformation, where the unit cell is compressed along z-axis, and expanded equally in x and y directions. In the latter two cases, we were also able to observe the same transformation. The critical values of strains this time were 0.27 and 0.29 for uniaxial and volume-conserving deformations, respectively. For orthophosphate, the diversity in stress tensor invariant values at the critical deformations was much higher than for the zinc phosphate. The values of stress tensor components along principal axes in xy-plane in the case of volume-conserving deformation turned out to be negative. This could be explained by the fact, that the crystal is much more interconnected, which should lead to a higher Young's modulus. As a result, the deformation in xy-plane, which is triggered by z-axis compression is expected to be much smaller for the considered crystal as compared to the mixture of initially weakly connected molecules. Additionally, in amorphous systems internal stresses could be relaxed through many more internal degrees of freedom than in a crystal.

The main difference between the considered amorphous and crystalline systems is that the transition in orthophosphate for all three deformation turns out to be reversible. In fact, the obtained structures return to their reference state at lower values of deformation or pressure, thus experiencing a hysteresis which was already reported in a study of this crystal subjected to hydrostatic compression [2]. Thus all of the phases obtained for the orthophosphate seem to be metastable, high-pressure phases, with higher enthalpies than the original crystal.

III. ROTATION OF THE ELASTIC TENSOR

If a system has monoclinic symmetry, thus having a parallelogram as a base and the third axis (for convenience let it be z-axis) perpendicular to the base, by rotating the system of coordinates around z-axis one can maximize and minimize the in-plane elastic constants C_{11} and C_{22} (not necessarily at the same time). From these values one can determine the stiffest and the softest in-plane directions. In our case the systems had triclinic symmetry after basin-restricted relaxations. However, the maximum deviation of the angle between any two unit cell vectors from 90° which we observed, was less than 3°. This obviously led to corrections to the calculated smallest and largest in-plane values of C_{11} and C_{22} of order 1% when compared to estimations based on assumption of orthorhombic unit cell. As a result we neglected these contributions given by the deviations of the unit cell angles from 90°, mostly because the analysis is supposed to be qualitative.

If we consider an isotropic solid and choose one axis (let it be z-axis for convenience), then the elastic tensor elements in the plane orthogonal to this axis would be independent with respect to rotations of the coordinate system. On the other hand, a highly anisotropic system would show a significant discrepancy between the minimal and maximal values of the in-plane C_{11} (or C_{22}) elastic constant when the rotation is applied. For simplicity of analytical derivation, we will consider only the case of orthorhombic system, but the equations could be easily generalized to any symmetry. When an orthorhombic system is rotated around z-axis by angle θ, the in-plane components of strain tensor evolve according to the following equations

$$\varepsilon'_{11} = \varepsilon_{11}\cos^2(\theta) + \varepsilon_{22}\sin^2(\theta) + \varepsilon_{12}\sin(\theta)\cos(\theta) \tag{1}$$

$$\varepsilon'_{22} = \varepsilon_{11}\sin^2(\theta) + \varepsilon_{22}\cos^2(\theta) - \varepsilon_{12}\sin(\theta)\cos(\theta) \tag{2}$$

$$\varepsilon'_{12} = 2(\varepsilon_{22} - \varepsilon_{11})\sin(\theta)\cos(\theta) + \varepsilon_{12}(\cos^2(\theta) - \sin^2(\theta)) \tag{3}$$

where ε_{ij} and ε'_{ij} are the components of strain tensor in the original and in the rotated coordinate system, respectively. By writing down the elastic energies in the two coordinate systems and by using Eqs. (1)-(3), one can show that the elastic tensor component C_{ii} within the plane would evolve according to the following equations

$$C'_{11}(\theta) = C_{11}\cos^4(\theta) + C_{22}\sin^4(\theta) + 2(C_{12} + C_{66})\sin^2(\theta)\cos^2(\theta) \tag{4}$$

$$C'_{22}(\theta) = C_{11}\sin^4(\theta) + C_{22}\cos^4(\theta) + 2(C_{12} + C_{66})\sin^2(\theta)\cos^2(\theta) \tag{5}$$

Let us focus on just one equation (let it be Eq. (4)). When rotated by 90°, $C'_{11}(\theta)$ becomes C_{22}. In the interval of rotations $0° < \theta < 90°$, $C'_{11}(\theta)$ has either a maximum or a minimum, and the corresponding rotation satisfies

$$\sin^2(\theta_\mathrm{m}) = \frac{C_{11} - (C_{12} + C_{66})}{(C_{11} + C_{22}) - 2(C_{12} + C_{66})}. \tag{6}$$

The value of the in-plane elastic constant at this angle is

$$C'_{11}(\theta_\mathrm{m}) = \frac{C_{11}C_{22} - (C_{12} + C_{66})^2}{(C_{11} + C_{22}) - 2(C_{12} + C_{66})} \tag{7}$$

Thus, depending on the balance between the four elastic constants involved in Eqs. (6) and (7), C'_{11} would satisfy either $\min(C_{11}, C_{22}) \leq C'_{11}(\theta) \leq C'_{11}(\theta_\mathrm{m})$ (when $2C' = (C_{11} - C_{12}) < C_{66}$ in a cubic system; there are several conditions for other symmetries) or $C'_{11}(\theta_\mathrm{m}) \leq C'_{11}(\theta) \leq \max(C_{11}, C_{22})$ (when $2C' > C_{66}$ in a cubic system).

In closed-packed metals, $\max(C_{11}, C_{22}) < C'_{11}(\theta_\mathrm{m})$. The values for $C'_{11}(\theta_\mathrm{m})/\min(C_{11}, C_{22})$, which characterizes the relative difference between the maximum and minimum values of C'_{11}, span from 1.03 (gold) to 1.25 (potassium). Thus, Au (and Ag as well) are very close in this regard to an isotropic solid, which would give a perfect unity. For ionic solids, $\min(C_{11}, C_{22}) > C'_{11}(\theta_\mathrm{m})$, which is the opposite trend compared to metals. In this case, we construct a measure $C'_{11}(\theta_\mathrm{m})/\max(C_{11}, C_{22})$. The well-known NaCl has a value 0.67, and CsI - a value of 0.75. For crystals with covalent bonding, the relation is the same as for ionic solids, however the values tend to be closer to unity: diamond has a value of 0.93, and cubic BN - 0.91. Layered structures like graphite and V_2O_5 fall into the same category and have values of the relation 0.79 and 0.77, respectively.

For the system which we considered in the current study, it turned out to be $\min(C_{11}, C_{22}) > C'_{11}(\theta_\mathrm{m})$ mostly because C_{12} is significantly smaller than C_{11}. $C'_{11}(\theta_\mathrm{m})/\max(C_{11}, C_{22})$ for the majority of configurations fall between 0.75 and 0.84. Just by itself this number does not give much insight into the structure and potential behavior under external stress. However, we can compare the out-of-plane elastic constant (C_{33} in our case) to the minimum and maximum values of the in-plane elastic constants. The values of C_{33} happen to be either slightly above $C'_{11}(\theta_\mathrm{m})$ or even below it. From these observations one could make a conclusion that our amorphous zinc phosphates seem to be overall softer along the direction of deformation when compressed uniaxially. In contrast to the initial interpretation leading to polymerization, this speaks more towards a cross-linked structure, which is "layered", and the effective bond strengths (effective force constants) along z-axis are overall weaker than the in-plane ones.

[1] S. V. Sukhomlinov and M. H. Müser, The Journal of Chemical Physics **146**, 024506 (2017).

[2] D. Shakhvorostov, M. H. Müser, N. J. Mosey, Y. Song, and P. R. Norton, Physical Review B **79** (2009), 10.1103/physrevb.79.094107.

[3] M. Gauvin, C. Minfray, M. Belin, G. Aquilanti, J. Martin, and F. Dassenoy, Tribology International **67**, 222 (2013).