

# Mechanical properties of zinc and calcium phosphates: Structural insights and relevance to anti-wear functionality

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Metal phosphates have a broad range of stiffnesses depending on the coordination number of the central cation and the chemical nature of the ligands. In addition, the increase of stiffness with pressure ranges from relatively little to quite dramatic, the latter being the case in particular for low-coordinated zinc phosphates containing hydroxyl terminations or large amounts of water. Here, we review recent results on stiffness and its pressure dependence of various metal phosphates ranging from simple model molecules for decomposition products of ZDDP, to thermal and tribo films produced from commercial lubricant packages via heating and rubbing. New results on the aging of zinc phosphate tribo films are presented as well. The softening of the films that occurred after exposing them to humidity can be easily rationalized in terms of the high-pressure experiments on model substances.

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## I. INTRODUCTION

In these proceedings, we review recent progress made on understanding the mechanical behavior of metal phosphates with an emphasis on zinc phosphates (ZPs). The interest in these materials stems from their ability to form thin protective films on rubbing surfaces. While ZPs are currently being phased out as anti-wear additives in commercial lubricants for environmental reasons, we believe that their interesting mechanical properties are relevant to their protective function. In the attempt to design new anti-wear additives, it may thus be beneficial to aim for molecules that respond to mechanical stress in a similar fashion as ZPs.

While the study of ZPs, in particular of zinc dialkyl dithiophosphates (ZDDPs) has traditionally focused on chemical pathways from the decomposition of ZDDPs to the film formation<sup>1</sup>, the mechanical properties of the formed films and how these relate to the local chemistry has received significant attention only over the last ten years. For example, Bec *et al.*<sup>2</sup> found that some zinc phosphates stiffen dramatically with pressure, Nicholls *et al.*<sup>3</sup> observed that films on top of asperities, where pressure attains its maximum values, are stiffest and have the largest degree of connectivity. In order to explain these, or related findings in tribology from atomistic principles, it has become common practice to mimic the experimental situations with computer simulations<sup>4-6</sup>. Based on *ab-initio* simulations of simple model molecules for ZDDP decomposition products, Mosey *et al.*<sup>7</sup> suggested that pressure plays a crucial role in the (fast) formation of protective films and that high pressure leads to the quasi-instantaneous formation of stiff networks. This theory and how it relates to many different experimental observations has been discussed in detail in Ref. [8].

A point that the crosslink theory<sup>7,8</sup> has not yet explicitly addressed is how the stiffness of a zinc phosphate can change without a coordination change on the metal

cation and how stiffness depends on ligands. In this article, we seek to fill this gap. For this purpose, we will summarize findings, mainly of an experimental nature, on the response of zinc and calcium phosphates to large stresses. This overview will be augmented by new data on how stiffness is affected by exposing ZP containing tribofilms for a long time to air and moisture.

## II. BACKGROUND AND THEORY

Metal phosphates tend to form networks in which anionic PO<sub>4</sub> tetrahedra are connected via metal cations<sup>9,10</sup>. Continuously increasing the connectivity of cations with the rigid anionic units can turn a material from an initially non-bonded viscoelastic system, with an open network structure, to a more densely packed and hence stiffer structure, as shown in the schematic of Fig. 1. The number of tetrahedra to which a cation is bonded varies and cannot be easily predicted. However, as a rule of thumb, one may expect that small cations with the ability to rehybridize, such as the transition metal zinc, can more easily adopt small (that is tetrahedral) and flexible coordination than other cations. For example, boron may have a lesser propensity to produce open networks than zinc, which may explain why wear tests with borate dialkylthiophosphate (BDDP) containing lubricants protected surfaces less from wear than those with ZDDP, despite the lower decomposition temperature of BDDP, which results in a higher film formation rate<sup>11</sup>.

An important issue may thus be how it is possible to control the stiffness of a tribo film. A phosphate network can be made harder by increasing the coordination on the cation. In some cases, it may be possible to achieve stiffening irreversibly via the application of high pressure, which occurs during asperity collision. However, even zinc tends to revert back to four-coordination during decompression after having adopted five and six-

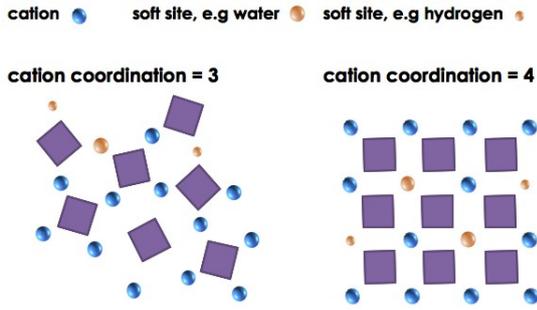


FIG. 1: Schematic representation of open and dense network formers in two dimensions. The squares represent qualitatively rigid units connecting different ions, such as tetrahedral  $\text{PO}_4$  units in metal phosphates.

coordinated structures at high pressures<sup>7,12</sup>, despite having stable six-fold coordination in pyrophosphates.

Softening structures can be achieved by reducing the chemical connectivity with network modifiers, such as hydrogen or hydroxyl terminations, which interrupt the chemical connectivity and thereby introduce soft spots into the system. However, once exposed to very large stresses, *all* atoms will be squeezed deep into the repulsive part of their interaction potentials. As a consequence, the stiffness becomes more and more simply a function of the electron density. At the origin of this behavior is the Pauli exclusion principle, which is reflected in the  $\rho^{3/2}$  term of density functional theory (DFT), where  $\rho$  is the density of electrons. As this term is the one in the DFT functional that grows the quickest with  $\rho$ , the term becomes the dominant contribution in the energy counteracting the term  $P/\rho$ , which expresses the coupling to external pressure  $P$ . Thus, soft sites induce “smartness” in a material, i.e., an extraordinary increase of the bulk modulus  $K$  with increasing  $P$ .

In their crosslink theory<sup>7,8</sup>, Mosey *et al.* argued that a pressure-induced increase in connectivity of zinc phosphate materials and the consequent increase in their stiffness constitute key ingredients to their formation and functionality as anti-wear films. They also discussed the role of network modifiers and speculated that calcium would be such a modifier due to its inability to form strong directed bonds. In the meantime, calcium has been shown to adopt a high coordination thereby forming stiff networks, so that the suggestion<sup>7,8</sup> of calcium being a softening network modifier needs to be corrected<sup>12</sup>. This correction, however, does not exclude the possibility of the existence of other network modifiers, which act in the fashion anticipated in Refs. [7] and [8]. For example, the presence of additional network modifiers would explain why anti-wear films that were obtained with lubricants containing Ca-based detergents were softer than those films derived from lubricant merely containing ZDDP<sup>13</sup>, although pure Ca-phosphates tend to be stiffer than Zn phosphates.

### III. EXPERIMENTAL RESULTS

#### A. Model compounds

A potential point of criticism to the idea of local stress triggering structural modifications to zinc phosphates on surfaces is that the macroscopic hardness of most materials is not sufficiently high to support the required stresses, which are in the vicinity of 5 GPa. To address this issue, Shakhvorostov *et al.*<sup>14</sup> presented Raman data on  $\alpha$ -orthophosphate of zinc, which was compressed on a copper foil in a flat punch experiment. In Fig. 2, we augment these data with a photograph of the sample from which the Raman spectra were collected. A change in the optical properties, which are sensitive to the *local* structure, is rather apparent.

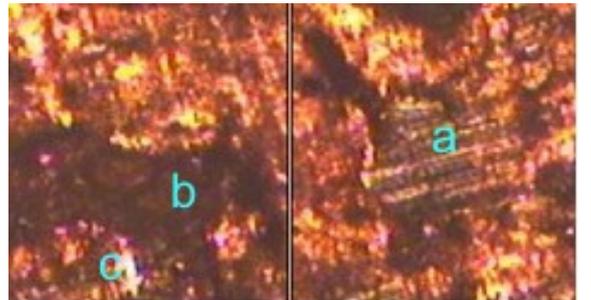


FIG. 2: Photograph of a zinc-phosphate film bearing copper foil that was exposed to high pressure in a flat punch experiment. Different areas can be identified. (a) Bare copper, (b) dark spots producing identical Raman spectra as  $\alpha$ -orthophosphate of zinc (AOZ), and (c) bright spots producing identical Raman spectra as that of AOZ having been exposed to pressures above 5 GPa. For the Raman spectra, we refer to Fig. 5 in Ref. [14].

From the experiment shown in Fig. 2, one can thus conclude that the desired pressures to invoke structural or chemical changes in the material can be induced on a material whose macroscopic hardness is less than the pressure at which the crystalline structure of zinc phosphate becomes thermodynamically unstable. Thus, the reactions can be induced on materials that deform plastically underneath. Moreover, one can see that a perfectly isotropic pressure is not required to induce the predicted coordination changes on zinc.

Fig. 3 summarizes recent results on the stiffness of various metal phosphates at ambient pressures. The trends are in very nice agreement with the first-principle simulations of Mosey *et al.*<sup>7</sup> on which the crosslink theory was based. From their equation of state, one can conclude the following values for the bulk moduli:  $K = 15$  GPa for the initial viscoelastic ZP fluid, which roughly coincides with the value found for  $\text{Zn}(\text{H}_2\text{PO}_4)_2$ ,  $K = 40$  GPa for the tetrahedral network formed after compression,  $K = 85$  GPa for five-coordinated ZP, and  $K = 130$  GPa for six-coordinated ZP. These trends are consistent with the results on metal phosphates that contain no, or small

amounts of, hydrogenation. Moreover, introducing network modifiers does decrease  $K$  quite substantially. For example, the stiffness of zinc pyrophosphate decreases from 80 GPa to 25 GPa by adding 1.3 molecules of  $H_2O$  per  $Zn_2P_2O_7 \cdot H_2O$  molecule. Thus, water leads to a dramatic reduction in stiffness when embedded in ZPs. We expect that other metal phosphates and modifiers will follow the same trend, in particular that the hydrolysis of metal phosphate networks with water leads to a specially strong reduction of stiffness.

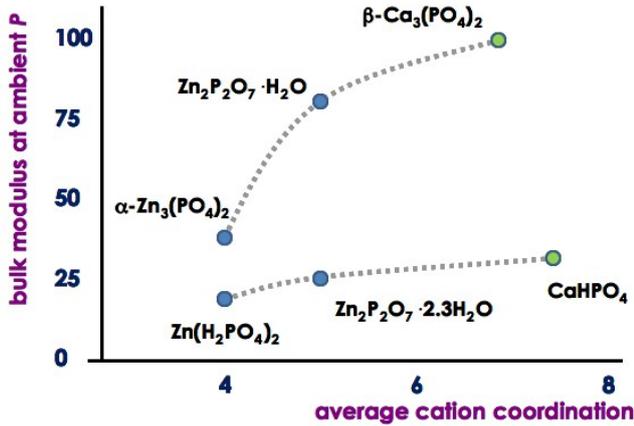


FIG. 3: Stiffness as a function of the average cation coordination for various metal phosphates. Data from Ref. [12].

In Fig. 4 one can see that those systems, which were compliant at ambient conditions, have a strong pressure dependence of the bulk modulus on pressure, i.e.,  $K' = dK/dp$  takes values much exceeding typical values of five<sup>12</sup>. Large values of  $K'$  are referred to as smart material behavior, because the material adjusts its response as a function of the external stimulus. For the materials studied here one may summarize that soft implies smart. We believe that this smartness is an important aspect for the functionality of zinc phosphates as anti-wear films.

A recent study<sup>15</sup> has confirmed the smart material effects observed on model compounds for thermal films. Thermal films contain a large fraction of pyrophosphates mixed with a small fraction of orthophosphates. What makes thermal films special is a measurable fraction of water in their original structure. Hydrolysis of the films during degradation of ZDDP has been mentioned in the literature previously<sup>16</sup>. The effect may not have been studied in more detail due to the belief that this might be insignificant for the properties of ZP films. However, it is well known from biological systems that water softens adsorbed layers<sup>17</sup>, and likewise significantly alters elastic and plastic response, not only in ZP model compounds, but also in tribo films as will be shown in the next section.

The fact that the mechanical response of the film material is affected by an instability of water molecules was confirmed in the high pressure experiment on thermal films, whose structure was studied *in situ* by means of infrared spectroscopy (IRS) and X-ray diffraction (XRD).

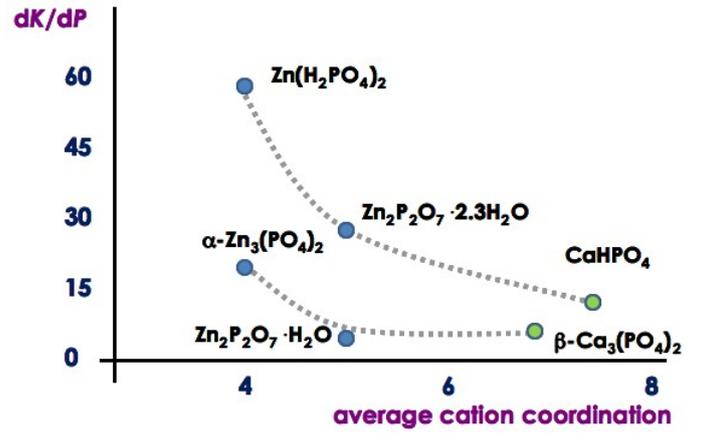


FIG. 4: The change of stiffness with pressure,  $K' = dK/dP$  for different compounds as a function of the average coordination of the metal cation. Data from Ref. [12].

The equation of state measured by XRD indicated an abrupt change in the density of thermal films at about 3.5 GPa; IRS then confirmed that the jump in density occurred at the same time as hydroxyl groups embedded in the crystal structure of phosphates changed their vibrational modes. This observation led to speculation that water can be squeezed out of the crystal structure by pressure. The pressure induced dehydration of *initially* soft thermal films might be a reason for the increased stiffness of the film on asperities under tribological contact observed earlier<sup>3</sup>. Squeezing out water via pressure can be seen as a new facet of the idea that pressure enhances networking, because eliminating soft sites leads to an increase in crosslink density. The experiments presented in the next section shall elucidate this point further.

## B. Aged tribofilms

While we would argue that the predictions of the crosslink theory made on the response of ZPs to stress can be seen as confirmed, the question arises to what extent the tested model substances reflect the behavior of real tribo films. Specifically, it would be interesting to know if softening network modifiers, such as water, have a similar effect on the elastic properties of tribofilms as on the model substances. To answer this question, we present data on anti-wear films that had been exposed to 14 months of air and humidity.

Our experiments were conducted using the IFM, which has the ability of in-situ imaging of the anti-wear film as well as measuring the stiffness of pads in both approach and withdrawal of the pads<sup>3</sup>. The original anti-wear film was produced using a Cameron-Plint reciprocating wear tester. The test conditions consisted of a rubbing time of 1 hr, at 100°C, with an applied load of 220 N and a frequency of 25 Hz under a fully flooded state. The base

oil contained 5 mM concentration of neutral di-isobutyl ZDDP. The resulting films were elongated parallel to the sliding direction and they had an indentation modulus of 100 GPa. After exposure to air and humidity for 14 months, small bumps were observed on the film, see Fig. 5.

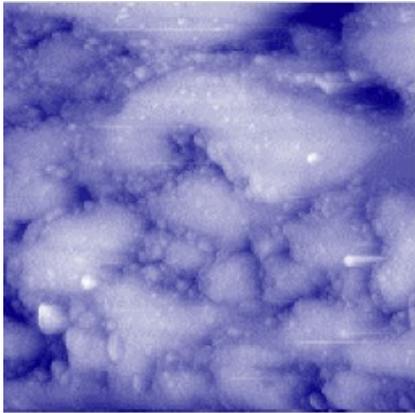


FIG. 5: An IFM height image where dark regions are lower than the brighter areas. The large antiwear pads elongated in the direction of rubbing. Note the small bumps located on the surfaces of the large antiwear pads. The linear dimension of the imaged region is 12  $\mu\text{m}$ .

The mechanical response of regular, i.e., non-bumpy area as well as that of two selected bumps to indentation are shown in Fig. 6. Locations on the anti-wear films without any apparent change in topography had an unchanged response to indentation, i.e., a fairly elastic response with a stiffness of 100 GPa, indicative of a film with high coordination on the Zn atoms, see curve A in Fig. 6. This high stiffness on the film is consistent with the assumption that the high loads during film formation created a highly-coordinated ZP film. In the approach curve, the bumpy positions, configurations B and C, have a much reduced indentation modulus of  $K \approx 30$  GPa. This value is consistent with those obtained for strongly hydrated ZPs. In one of the two curves on the modified positions, namely curve B, no plastic deformation is apparent in the approach curve - yet, upon withdrawal,  $K$  has increased to a value of 63 GPa. Such stiffening requires that a major modification of the film occurred during indentation, because “moderate modifications” such as dislocation motion does not significantly alter stiffness. In curve C, non-elastic response is apparent in the approach curve as well as in the image shown. This time, the stiffness during withdrawal is even higher than that obtained from the previous withdrawal curve. The indentation results in the almost complete recovery of the original modulus.

The interpretation of the result shown in Fig. 6, curve C, is that the very high contact pressures caused chemical transformations of the sort discussed in Ref.<sup>15</sup> involving loss of water and/or change in hydroxyl terminations, and a subsequent stiffening of the film only after sig-

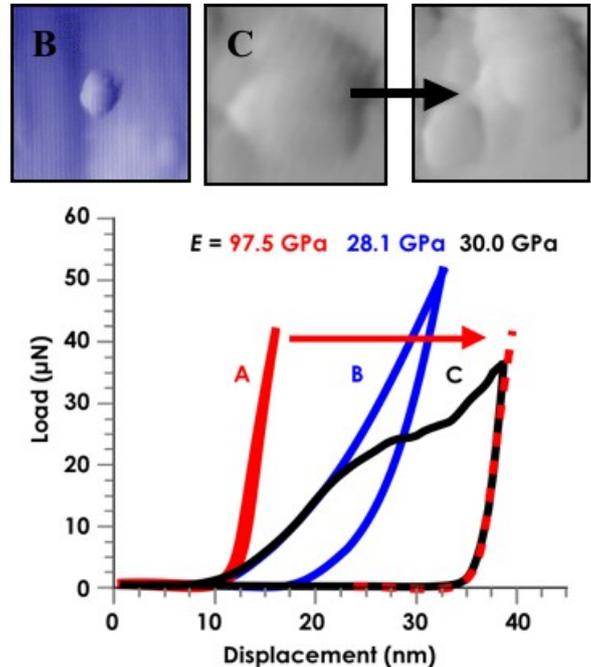


FIG. 6: The load versus displacement curves for different locations on the aged film. Curve A is representative of an area of the film where no bumps existed (likely unaltered) and has an elastic response identical to that measured previously for non-aged films<sup>3</sup>. Curves B and C are displacement curves taken on the altered areas of the film; the bumps show in images B and C.

nificant plastic deformation occurred which is visible in the IFM image. The residual (and smaller) plastic deformation that appears in the force displacement curve for Fig. 6 was not readily imaged and is therefore not illustrated. Differences in water/hydroxyl content and depth of the modified region might be the origin of the difference in behaviour between these two “bumps” on the anti-wear film.

#### IV. CONCLUSIONS

In this paper we recapitulated recent theories and experiments on how cation coordination, side groups, and hydration in metal phosphates lead to their rich mechanical properties. New experiments on hydrated films and their irreversible response to stress were presented as well. These experiments provide new ammunition for the idea that compressive stress can increase stiffness by increasing the crosslink density in a system via elimination of water as a softening network modifier.

Due to the new results presented here, it is tempting to speculate that films on top of asperities are less strongly hydrated than those in the valleys. The high contact pressures and temperatures would lead to the dehydration and thus ultimately enhance the stiffness of anti-wear pads residing on top of asperities, e.g., by reducing

$\text{Zn}_2\text{P}_2\text{O}_7 \cdot 2.3\text{H}_2\text{O}$  into  $\text{Zn}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$  or  $\text{Zn}_2\text{P}_2\text{O}_7$ . This speculation would be consistent with earlier nanoindentation experiments<sup>13,18</sup> and be alternative and/or additional reasons to those discussed earlier in the crosslink theory<sup>7,8</sup>.

While this paper is concerned with the stiffness of model zinc phosphates and zinc phosphate containing anti-wear films rather than with their hardness, one may speculate that hardness also depends on the cation coordination and the chemical nature of the ligands, which become incorporated into the film. Support for this expectation comes from nanoindentation experiments, in which it was found that the hardness of ZDDP and fluorinated ZDDPs derived anti-wear films was significantly reduced in the presence of antioxidants<sup>19</sup>. However, fu-

ture studies are needed to come to a more detailed picture.

In regard to the anti-wear function of ZDDP's decomposition products, we believe that it is based to a significant degree on the ability of the film material to stiffen rapidly under pressure<sup>2,12,15</sup>: The stiffening reduces the effect of inertial confinement, which allows the substrate to deform while interacting with a relatively soft film, thus reducing the maximum stress during the collision of two asperities. Material with significant stiffening behaves elastically in analogous manner to a system of various layers of different stiffness, thereby producing what one could term a "helmet effect". We hope that these insights will help guide the design of new generation anti-wear additives.

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- <sup>1</sup> H. Spikes, *Tribol. Lett.* **17**, 469 (2004).
- <sup>2</sup> B. S. Bec, A. Tonck, J. M. Georges, R. C. Coy, J. C. Bell, and G. W. Roper, *Proc. R. Soc. London A* **455**, 4181 (1999).
- <sup>3</sup> M. A. Nicholls, T. Do, P. R. Norton, G. M. Bancroft, M. Kasrai, T. A. Capehart, Y.-T. Cheng, and T. A. Perry, *Tribol. Lett.* **15**, 241 (2003).
- <sup>4</sup> J. A. Harrison, G. Gao, J. D. Schall, M. T. Knippenberg, and P. T. Mikulski, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **366**, 1469 (2008).
- <sup>5</sup> O. Braun and A. Naumovets, *Surface Science Reports* **60**, 79 (2006).
- <sup>6</sup> M. H. Müser and M. U. nd M. O. Robbins, *Adv. Chem. Phys.* **126**, 187 (2003).
- <sup>7</sup> N. J. Mosey, M. H. Müser, and T. K. Woo, *Science* **307**, 1612 (2005).
- <sup>8</sup> N. J. Mosey, T. K. Woo, M. Kasrai, P. R. Norton, G. M. Bancroft, and M. H. Müser, *Tribol. Lett.* **24**, 105 (2006).
- <sup>9</sup> R. K. Brow, D. R. Tallant, S. T. Myers, and C. C. Phifer, *Journal of Non-Crystalline Solids* **191**, 45 (1995).
- <sup>10</sup> R. K. Brow, *Journal of Non-Crystalline Solids* **263-264**, 1 (2000).
- <sup>11</sup> Y. Wang, J. Li, and T. Ren, *Industrial Lubrication and Tribology* **61**, 33 (2009).
- <sup>12</sup> D. Shakhvorostov, M. H. Müser, N. J. Mosey, Y. Song, and P. R. Norton, *Phys. Rev. B* **79**, 104303 (2009).
- <sup>13</sup> M. A. Nicholls, G. M. Bancroft, P. R. Norton, M. Kasrai, G. De Stasio, B. H. Frazer, and L. M. Wiese, *Tribol. Lett.* **17**, 245 (2004).
- <sup>14</sup> D. Shakhvorostov, M. H. Müser, N. J. Mosey, D. J. Munoz-Paniagua, G. P. amd Y. Song, M. Kasrai, and P. R. Norton, *J. Chem. Phys.* **128**, 074706 (2008).
- <sup>15</sup> D. Shakhvorostov, M. H. Müser, Y. Song, and P. R. Norton, *J. Chem. Phys.* **XXX**, XXX (XXX).
- <sup>16</sup> P. A. Willermet, D. P. Dailey, R. O. Carter III, P. J. Schmitz, and W. Zhu, *Tribol. Int.* **28**, 177 (1995).
- <sup>17</sup> S. Lee and N. D. Spencer, *Science* **319**, 575 (2008).
- <sup>18</sup> O. L. Warren, J. F. Graham, P. R. Norton, J. E. Houston, and T. A. Michalske, *Tribol. Lett.* **4**, 189 (1998).
- <sup>19</sup> A. Somayaji, R. Mourhatch, and P. B. Aswath, *J. Nanosci. Nanotechno.* **7**, 4378 (2007).