

# Energy dissipation via quantum chemical hysteresis during high-pressure compression: A first-principles molecular dynamics study of phosphates

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(Received 2 May 2005; published 25 August 2005)

The chemomechanical response of triphosphates (TPs) and zinc phosphates (ZPs) to changes in pressure  $p$  and temperature  $T$  is studied through first-principles molecular dynamics. The maximum values of  $p$  ( $>20$  GPa) and  $T$  ( $\approx 1000$  K) are chosen to mimic roughly the extreme conditions to which phosphates may be exposed during their role as engine antiwear films. In all systems, atoms undergo pressure-induced changes in coordination number. Upon decompression, these chemical changes are partially reversible but nevertheless show strong hysteresis effects. This leads to significant energy dissipation, which contributes to the high friction coefficients of ZP antiwear pads. ZPs remain a covalently cross-linked network after decompression, while TPs revert to a disconnected state. The decompressed TPs have a larger bulk modulus ( $\approx 35$  GPa) than the uncompressed TPs ( $\approx 27$  GPa). This increase is due to symmetry-breaking proton transfer reactions, which are irreversible on the time scale of the simulation. Temperature has little effect on the results.

DOI: [10.1103/PhysRevB.72.054124](https://doi.org/10.1103/PhysRevB.72.054124)

PACS number(s): 62.20.Qp, 62.50.+p, 82.20.Wt, 64.30.+t

## I. INTRODUCTION

The behavior of phosphates under extreme conditions is of interest in engineering and physical disciplines ranging from planetary science to tribology, the science of surfaces in relative motion. For example, various phosphates have been found in meteoroids, where they exhibit spectra indicative of metastable phases. These phases are formed through exposure to high pressures.<sup>1,2</sup> Phosphates such as  $[\text{Pb}_3(\text{PO}_4)_2]$  (Ref. 3) and  $(\text{TiH}_2\text{PO}_4)$  (Ref. 4) also find applications as ferroelastics. All these examples show that many metal phosphates exhibit shape- and stress-memory properties.

In tribology, the interest in phosphates stems from the presence of zinc phosphates (ZPs) in antiwear films formed on automobile powertrain components.<sup>5</sup> ZPs are known to adhere quickly to steel or cast iron under rubbing conditions, thereby forming so-called antiwear pads (AWPs). The mechanical and chemical properties of the AWP vary with their location on the surface. AWP located on top of asperities are typically harder and show spectra reminiscent of longer ZP chains than those found in the valleys between asperities.<sup>6</sup>

For a long time, the predominant opinion in the literature was that the AWP form via complicated, surface-mediated reactions in which iron or other metals act catalytically.<sup>7</sup> This opinion has been challenged recently by first-principles molecular dynamics simulations.<sup>8</sup> It was suggested that high pressures transform the ZPs into a chemically connected network where zinc plays the role of the network-forming agent by altering its coordination number and geometry. Although chemical changes occur within the ZPs during the release of the pressure, the system remains in a connected state as long as enough zinc atoms are present. Similar networks may also be formed in metal phosphates if zinc is replaced by another cation that exhibits flexible coordination.

While ZP AWP are highly effective, albeit environmentally problematic antiwear agents, they also lead to signifi-

cant energy dissipation and friction. This is not always an undesirable effect. For example, high friction in clutches leads to a better transmission of forces.<sup>9</sup> The formation and antiwear functionality of ZP AWP have been discussed elsewhere.<sup>8</sup> A detailed comparison between the results of our earlier study and tribological experiments has also been made.<sup>10</sup> In this paper, we discuss mechanisms that may be responsible for a large degree of energy dissipation in (zinc) phosphate AWP. In particular, we focus on how dissipation is achieved through the chemomechanical response of (zinc) phosphates to time-dependent pressures. The relevant mechanisms occur through pressure-induced changes in coordination at specific atoms in these systems.

It is certainly well known that many solids or glasses undergo structural and chemical changes in response to variations in external pressure. With the notable exception of hexagonal close-packed or face-centered cubic solids, e.g., rare gas solids and many simple metals, most systems undergo an increase in coordination number when the pressure becomes sufficiently large. A prominent example is carbon, which changes from a tricoordinate to a tetracoordinate state during the transformation of graphite to diamond with high pressure and heat. The conversion of hydrocarbon chains into graphite, i.e., two C–C bonds per carbon atom to three C–C bonds per carbon atom, is also believed to play a role in various tribological systems, such as artificial hip implants.<sup>11</sup> Similar behavior has also been observed in simulations of alkyl chains that contained acetylene moieties, where the formation of cross-linked networks occurred through changes in the coordination number of the  $sp$ -hybridized carbon atoms in response to compression and shear.<sup>12</sup>

Unlike carbon-based materials, many systems undergo changes in coordination number that are reversible on relatively short time scales. The inverse reactions, however, usually occur at smaller pressures than the original reaction.

This implies a hysteresis, which in turn leads to a loss of energy during each compression and decompression (*c/d*) cycle. In this paper, we will quantify the energy loss per *c/d* cycle for a small system composed of two triphosphate ( $\text{P}_3\text{O}_{10}\text{H}_5$ ) molecules. We will also analyze unpublished data on ZP systems ( $\text{ZnP}_5\text{O}_{18}\text{H}_9$ ) studied previously.<sup>8</sup>

Compression and depression loops of increasing and decreasing pressure must be expected to occur in engines during asperity collision. For a short period of time, the maximum pressures may reach the theoretical yield stress of the underlying substrate due to inertial confinement of the AWP and the surface material. Once dislocation motion and plastic deformation occur within the substrate, the pressure will drop quickly to below the experimentally observed yield stress. As demonstrated in our previous study,<sup>8</sup> many chemical transformations can occur in this short time period. Here, we are concerned with the relationship between these transformations and energy dissipation. Phosphates are of interest in scientific areas other than tribology, such as those mentioned at the beginning of this paper. This constitutes an additional motivation for the present high-pressure investigation of phosphates in their own right.

In the following section, we will briefly review the methodology employed in this study. Section III contains the results. Conclusions are drawn in Sec. IV.

## II. METHOD AND MODEL

We employ a similar strategy in this study as in our previous paper,<sup>8</sup> i.e., a system consisting of (zinc) phosphates is compressed isotropically to pressures,  $p$ , greater than 20 GPa and then decompressed. Periodic boundary conditions are employed in all three dimensions, and the simulation cell is allowed to fluctuate as an arbitrary parallelepiped. The pressure is changed at the slowest rate currently amenable to *ab initio* simulations, which is  $\pm 10$  GPa/ps for our system of interest. This compression rate is higher than that expected to occur in car engines. However, we decreased this value by a factor of 4 without any significant effect on the behavior of the system. To estimate the rate of pressure change in sliding contacts, one may assume conservatively that two surfaces slide at 10 m/s in a car engine, and that two asperities undergo a dramatic pressure change (from 0 to 20 GPa) when they move from being separated by 10 nm to being in intimate mechanical contact. This implies that we are off by only about 3 orders of magnitude in compression rate. We feel strongly that rate effects are small, because even dramatic temperature changes barely alter the pressure at which chemical reactions occur in our simulations. Of course, our calculations would not apply to situations in which asperity collision is sufficiently slow to allow the phosphates to be come squeezed out of the contact.

The initial configuration consists of small, disconnected phosphate molecules ( $\text{P}_3\text{O}_{10}\text{H}_5$ ). They are heated up to 1000 K, tempered for a short period of time, and quenched down to lower temperatures, typically 300 K. The changes in coordination number reported below occur at pressures that are rather insensitive to the details of the initial structure. This makes us confident to claim that no dramatic consequences

in the high-pressure behavior should be expected from a better equilibrated initial structure. Despite having only two molecules in the simulation cell, size effects (related to changes in bonding) should also be small because we have not noticed any significant size effects in the simulation of ZPs, where larger systems were considered. Including or neglecting zinc atoms was the only modification that led to rather dramatic changes in the chemomechanical response of the system.

All *ab initio* molecular dynamics simulations were performed with the CPMD program.<sup>13</sup> Density functional theory was used throughout with the exchange-correlation functional of Perdew, Burke, and Ernzerhof.<sup>14</sup> Core electrons on all atoms were represented by norm-conserving pseudopotentials<sup>15</sup> and the valence states were expanded as a set of plane waves at the  $\Gamma$  point up to a cutoff of 120 Ry. Test calculations on simple phosphate systems showed that pressures were converged with respect to basis set size. In general, pressures calculated with a plane-wave cutoff of 120 Ry were within 0.2 GPa of those calculated with a cutoff of 200 Ry. This level of accuracy is adequate for the purposes of the simulations performed here. A time step of 2.0 a.u. and a fictitious electron mass of 800 a.u. were used in all simulations reported here. More recent simulations performed with a fictitious electron mass of 400 a.u. exhibit behavior that is virtually identical to that reported below. To give the reader an idea of the computational effort associated with the calculations, we note that completing one full *c/d* cycle with a maximum pressure of 32.5 GPa required approximately 2 weeks of CPU time on a cluster of 24 Compaq Alpha ES40 computers running at 833 MHz.

## III. RESULTS

### A. Equation of state, hysteresis, and dissipation

The equation of state for a system composed of two triphosphate (TP) molecules is shown in Fig. 1. One can observe a relatively large volume for the initial configuration, that is, in the beginning of the initial compression run. This system consists of two disconnected TP molecules, which have been relaxed as described above and in which hydrogen atoms can still be associated with individual molecules. After a first *c/d* cycle, the low-pressure volume turns out to be smaller than during the initial compression. In all subsequent runs, we find a well-defined equation of state, where the curves associated with compression and decompression lie on top of each other within the statistical error, except for the pressure range  $18 \text{ GPa} < p < 26 \text{ GPa}$ . In that regime, a hysteresis is clearly borne out. This hysteresis is a result of P–O bond formation and dissociation. These processes are discussed in Sec. III C.

The surface area enclosed between the two curves can be interpreted as the energy that is dissipated by the system each time it undergoes such a pressure loop during asperity collision. We are currently not in a position to estimate how much this hysteresis contributes to the friction coefficient. Such a calculation will probably require simulations at a much more coarse-grained scale in which one can assess how many TPs undergo the hysteresis per load and slide distance. However,

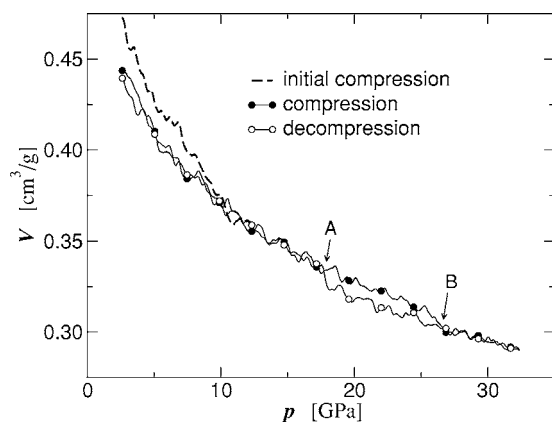


FIG. 1. Volume of the pure phosphate system (TPs) as a function of pressure. An initial compression cycle and a subsequent compression and decompression cycle is shown. A hysteresis occurs in the pressure range  $18 \text{ GPa} < p < 26 \text{ GPa}$ , indicated by points A and B. The initial system was compressed up to 32.5 GPa; however, it is only plotted up to 12.5 GPa for clarity. Beyond this point the curves for the initial compression and subsequent compression cycle essentially overlapped.

it is possible to estimate the generated heat  $\Delta Q$  per c/d cycle from the hysteresis, which turns out to be  $\Delta Q \approx 17.5 \text{ kJ/mol}$ . Using a value for the specific heat of TPs calculated through molecular dynamics simulations of  $c_p \approx 500 \text{ J/mol/K}$  and a molar mass of  $257.95 \text{ g/mol}$ , this corresponds to an increase in temperature of  $\Delta T \approx 36 \text{ K}$ , if one assumes that the heat remains confined locally. This defines a strict upper bound for the local temperature increase per c/d cycle due to reversible coordination changes in TPs.

Given a thermal conductivity of  $\kappa = 10^{-2} \text{ W/cm}^2 \text{ K}$ ,<sup>16</sup> we also obtain a rough estimate for the temperature diffusion coefficient  $D_T = \kappa / \rho c_p$  of  $D_T \approx 2 \times 10^{-7} \text{ m}^2/\text{s}$ . Note that this is a very rough guess, because we treated the nuclei as classical particles in our calculation of  $c_p$ . We expect that the true value of  $c_p$  is lower by a factor of approximately 2, and hence the true  $D_T$  approximately twice as large as our values stated above because the degrees of freedom associated with covalent bonds will be frozen in at temperatures below 1000 K. Given a typical thickness of  $d \approx 100 \text{ nm}$  for AWP, one can estimate a characteristic time  $\tau_c = d^2 / D_T \approx 50 \text{ ns}$  required for the temperature to diffuse from the compressed and decompressed molecule to the metal. Of course, these calculations are highly qualitative, but they would allow one to obtain a rough estimate of the contribution of the chemical hysteresis mechanism to the friction force, if one knew the mean time between asperity collisions and the amount of material subjected to the required pressures. Unfortunately, it appears presently impossible to make more reliable predictions without a distinctly more sophisticated model than that used here. Such an analysis is entirely beyond the scope of this study, which already required quite significant CPU power.

So far, the discussion has been limited to the case of pure phosphates. However, qualitatively similar equations of state can be seen in ZPs such as shown in Fig. 2, and Fig. 1 in Ref. 8. In ZPs, however, two hystereses are found instead of one.

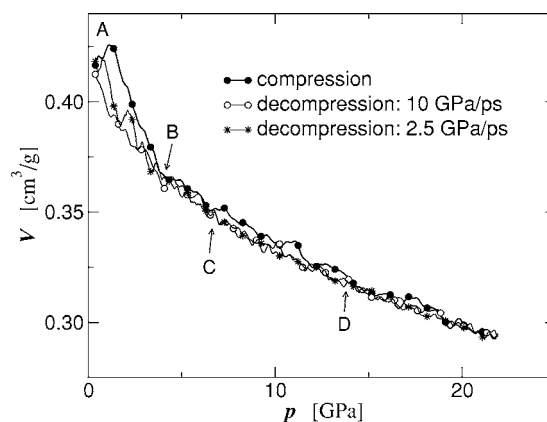


FIG. 2. Volume of the zinc phosphate system as a function of pressure. Only steady-state compression and decompression cycles are shown. A hysteresis is present at low pressure, between points A and B, and at high pressure, indicated by points C and D.

The loops occur at high ( $6 \text{ GPa} < p < 14 \text{ GPa}$ ) and low ( $0 \text{ GPa} < p < 4 \text{ GPa}$ ) pressures. The high-pressure hysteresis will be discussed first. It contains an area  $\Delta Q_h = 16.9 \pm 0.4 \text{ kJ/mol}$ , which is rather independent of the rate of compression. As discussed further below, we expect a logarithmic rate correction to the value of  $\Delta Q_h$ . The high-pressure hysteresis is due to the dissociation and formation of Zn–O bonds.

The loop at low  $p$  corresponds to  $\Delta Q_l = 30.1 \text{ kJ/mol}$  if compression and decompression occur at a rate of  $10 \text{ GPa/ps}$ . This value was reduced to  $\Delta Q_l^{\text{slow}} = 19.7 \text{ kJ/mol}$  when the decompression rate was decreased to  $2.5 \text{ GPa/ps}$ . This is entirely consistent with a linear response scenario, as one may argue that 1/4 of the hysteresis during compression and the full hysteresis during decompression are kept in the loop. This would mean that one should expect  $\Delta Q_l^{\text{slow}} \approx 5 \Delta Q_l / 8$ , which is certainly obeyed by our data within the statistical error.

The low-pressure hysteresis in ZPs is absent in TPs. This loop is not related to chemical changes, but rather to more subtle changes in the coordination geometry of the zinc. Since these rearrangements involve larger length scales than the quantum chemical processes, the number stated above for  $\Delta Q_l$  at the compression rate of  $10 \text{ GPa/ps}$  can be seen only as a rough estimate, given the small sizes of our systems. It is nevertheless tempting to speculate that the dissipation processes, or more precisely, the damping processes at low pressures, also contribute to dissipation in sliding contacts. Moreover, they may play an important role in the application of ZPs as thermal insulators in dental applications.<sup>16</sup>

From our simulations, we can deduce a characteristic relaxation time  $\tau_{\text{rel}} \approx \mathcal{O}(0.1 \text{ ns})$ . This means absorption will be high for a thermal energy  $k_B T_E = h / \tau_{\text{rel}} \approx 500 k_B K$ , where  $k_B$  is the Boltzmann constant. Since partial charges reside on the atoms in these systems, i.e., negative charges on oxygen and positive charges on zinc and phosphorus, both phonons and photons will be damped strongly when they possess thermal energies.

## B. Local dynamics

In TPs, the molecular hysteresis is due to the pressure-dependent formation and rupture of P–O bonds between

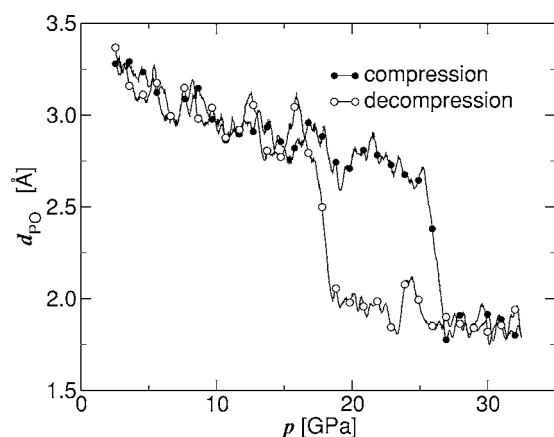


FIG. 3. Bond lengths between the phosphorus and oxygen atoms mediating the chemical cross-linking between two adjacent triphosphate molecules.

neighboring TP molecules. The distance between the phosphorus and oxygen atoms involved in bond formation,  $d_{PO}$ , is given in Fig. 3 as a function of pressure. During compression,  $d_{PO}$  decreases abruptly from 2.7 to 1.8 Å when a threshold pressure of 26 GPa is surpassed. This process is reversible and  $d_{PO}$  increases sharply from 2.0 to 2.9 Å at 16 GPa during decompression. This demonstrates that the bond formation- and dissociation processes are strongly dependent upon the external pressure. The pressures at which these transitions occurred correspond to the endpoints of the hysteresis in the equation of state for the TPs shown in Fig. 1.

The high-pressure hysteresis in the ZPs also arose from pressure-induced changes in coordination number and bonding. In that case, the reactions occur at the zinc atom and involve the collective motions of all oxygen atoms bonded to zinc. Consequently, the transitions responsible for the hysteresis occur more slowly than in TPs. Nonetheless, the concept of hysteresis through changes in coordination number is evident in both systems.

Dynamic instabilities of atoms (micro-“pops”) similar to those examined here have been discussed previously within the framework of simple boundary lubricants.<sup>18,19</sup> In those systems, current atomic positions become unstable suddenly due to sliding rather than compression. Once unstable, the atoms move quickly into the nearest energy minimum. Processes of this kind take place at various length scales and with different degrees of collectivity; see, for instance, Refs. 20,21. They generally lead to a rate dependence of dissipation that is relatively independent of the compression rate except for logarithmic corrections.<sup>18,19,22</sup> This rate dependence is rationalized most easily in terms of Eyring theory.

In the studies of simple boundary lubricants, the jumps or “micro-pops” of atoms are also due to atoms moving sud-

denly by a distance of approximately 1 Å. The mechanisms discussed here are similar, albeit based on a much more complex potential energy surface. Most importantly, the instabilities induced in the phosphates reported here are triggered by quantum chemical processes that cannot be cast easily in terms of classical, nonreactive force fields. In tribological simulations, reactive force fields have only been used for relatively simple hydrocarbons.<sup>12,23</sup>

### C. Local structure

The most important, pressure-induced chemical changes in TPs are shown in Fig. 4. At a relatively low pressure of  $p \approx 3.5 \pm 0.5$  GPa, an irreversible proton transfer reaction occurs. This reaction breaks the stoichiometric symmetry between the two molecules. Once this reaction has taken place, protons do not revert back to their initial positions on the time scales of the simulation. The reaction is endothermic, with the optimized products less stable than the initial structure by 20.6 kJ/mol. However, given the small difference in energies, a non-negligible fraction of the symmetry-broken systems may exist in thermal equilibrium with the initial state.

The symmetry-breaking proton transfer increases the bulk modulus of the system, as one can see from the slope in the  $p(V)$  diagram in Fig. 1. The bulk modulus  $B = \partial p / \partial \ln V$  can be read off Fig. 1, and it turns out to be  $B \approx 27$  GPa for the initial, low-pressure configuration and  $B \approx 35$  GPa for the configuration in which proton transfer has occurred. This value of 35 GPa is still much smaller than if zinc was present, in which case one obtains roughly 50 GPa at small and 85 GPa at intermediate pressures.<sup>8</sup>

It is tempting to speculate that proton transfer reactions may contribute to the work of hardening other phosphates when they are compressed to moderate pressures of up to 3 GPa. However, slower compression rates are used in (diamond anvil) experiments and the transition will occur at somewhat lower values of  $p$  than in the simulations.

At 26 GPa, the chemical connectivity is increased, as shown in Fig. 4(b). In this reaction, two phosphorus atoms become bonded through an oxygen. One of these phosphorus atoms, specifically the one bearing a positive charge due to proton transfer, becomes pentacoordinate, while the other remains in a tetracoordinate state. This process appears to occur predominantly at the end groups, which implies a polymerization of the TPs rather than the formation of a network. This can be understood through the antibranching rule,<sup>24</sup> which states that phosphates adopt linear structures in preference to branched or cyclic geometries.

Snapshots of the simulation cell are shown in Fig. 5. One can see that the two molecules undergo a reaction akin of a

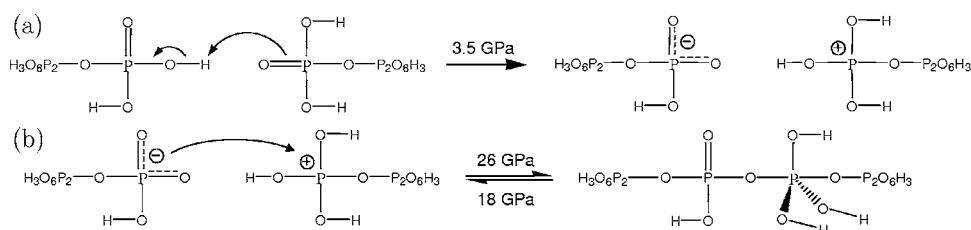


FIG. 4. (a) Schematic representation of the proton transfer reaction at  $p \approx 3.5 \pm 0.5$ . (b) Local chemical structure of the disconnected TPs (left) and the connected TPs (right).



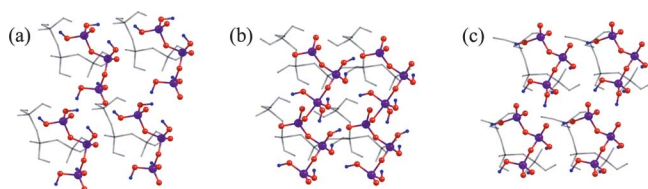


FIG. 5. (Color) Snapshots of TP at different pressures. The same simulation cell is represented repeatedly to visualize more clearly the effect of crosslinking. (a) Low-pressure configuration before the initial compression run. (b) Configuration at  $p > 26$  GPa. (c) Low-pressure configuration after decompression. Atoms in the uppermost layer of molecules are shown in a ball-and-stick representation. In this layer, oxygen, phosphorus, and hydrogen are represented by large red, large purple, and small blue circles, respectively. Atoms in underlying layers are represented only as sticks.

polymerization, i.e., one linear phosphate molecule is formed that stretches throughout the simulation cell. The cross-links, however, disappear when the pressure drops below 18 GPa. The important difference with respect to Fig. 2 in Ref. 8, which shows a similar set of snapshots for ZPs, is that ZPs remain in a moderately connected network after decompression.

#### IV. CONCLUSIONS AND DISCUSSION

We have discussed the chemomechanical changes that triphosphates (TPs) undergo when exposed to large pressures. This behavior was compared to that of zinc phosphates (ZPs). The TPs show two important pressure-induced chemical reactions. At  $p \approx 3.5$  GPa, a proton transfer reaction takes place, which leads to a stoichiometric symmetry breaking of the two TP molecules in the simulation cell. The proton transfer is irreversible on the time scale of the simulation and leads to a hardening of the system from  $B \approx 27$  GPa to  $B \approx 35$  GPa. At  $p \approx 26$  GPa, a polymerization reaction occurs in which terminal phosphate groups become bridged via an

oxygen atom. One of the two phosphorus atoms involved in the polymerization changes from a tetracoordinate to a pentacoordinate state. This process is reversible at  $p \approx 18$  GPa upon decompression. The resulting hysteresis in the equation of state indicates that the heat lost during each compression and decompression run is 17. (5) kJ/mol. In contrast to TPs, pressure-induced structural changes in ZPs at high pressures are dominated by coordination number changes at zinc rather than phosphorus. The resultant bond dissociation and formation processes may contribute significantly to energy dissipation under the high pressures experienced microscopically in sliding contacts, such as in automobile engines or transmissions.

The quantum chemical dissipation mechanisms discussed in this work will only be activated under extreme pressure conditions. However, phosphates also show high dissipation under less extreme conditions, as demonstrated recently in a quartz microbalance experiment.<sup>25</sup> The good thermal insulation properties of ZP glasses, used for instance in dental medicine,<sup>16</sup> also point to strongly anharmonic or dissipative dynamics in ZP glasses at small pressures. The responsible mechanisms may be related to the hysteresis observed in our systems at  $p < 4$  GPa, which showed distinct signs of being a linear-response effect. However, due to the limitations that first-principles calculations impose on system sizes, we are not yet in a position to make very reliable numerical predictions regarding the frequency-dependent mechanical response. This would require simulations based on classical force fields.

#### ACKNOWLEDGMENTS

The Natural Science and Engineering Research Council of Canada and General Motors R&D are acknowledged for providing financial support. Computational resources were made available by the Canadian Foundation for Innovation, SHARCNet of Canada, and the Academic Development Fund at the University of Western Ontario.

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