High-Pressure Chemistry

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The Chemical Imagination at Work in *Very* Tight Places

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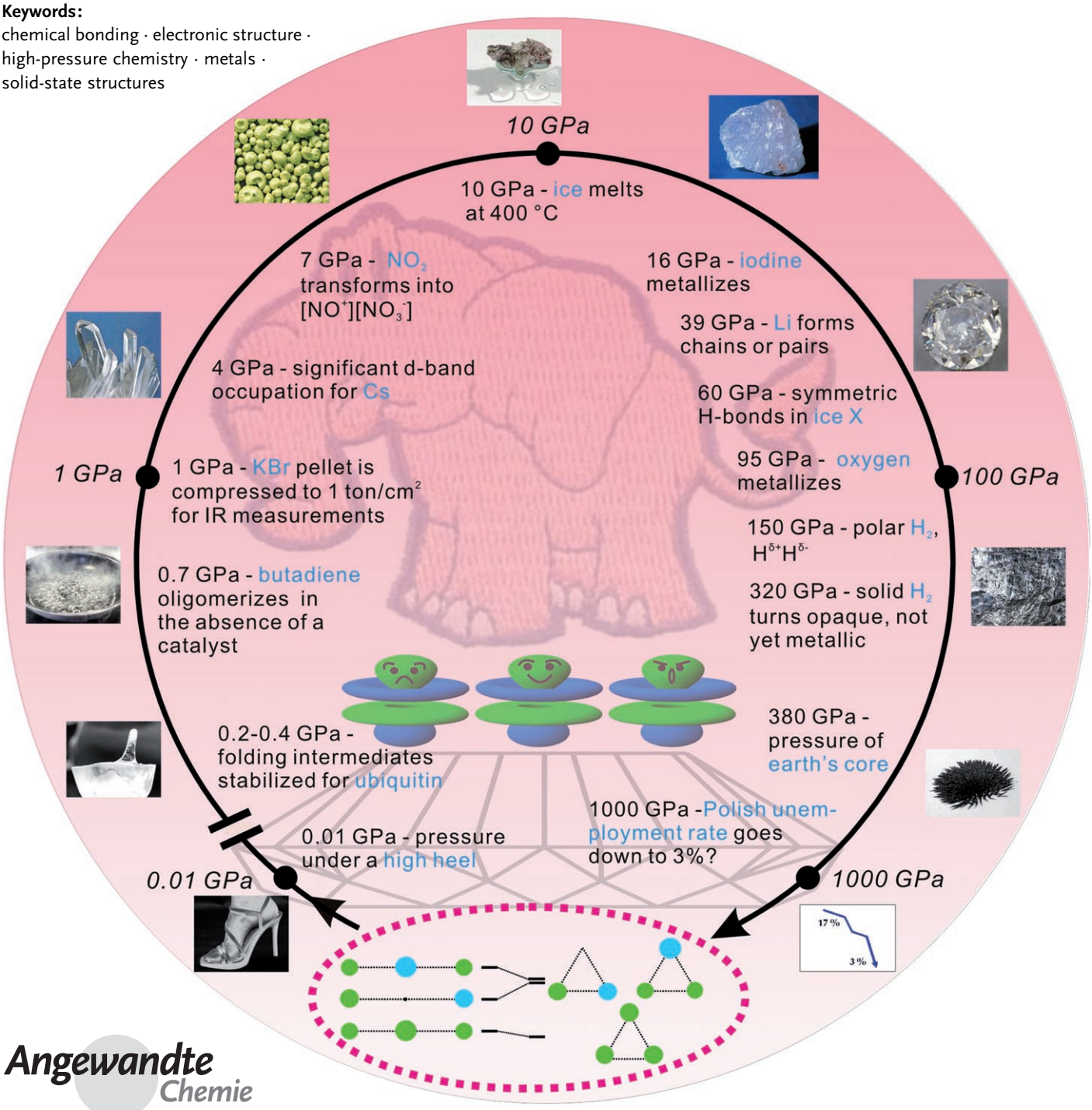

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Diamond-anvil-cell and shock-wave technologies now permit the study of matter under multimegabar pressure (that is, of several hundred GPa). The properties of matter in this pressure regime differ drastically from those known at 1 atm (about 10^5 Pa). Just how different chemistry is at high pressure and what role chemical intuition for bonding and structure can have in understanding matter at high pressure will be explored in this account. We will discuss in detail an overlapping hierarchy of responses to increased density: a) squeezing out van der Waals space (for molecular crystals); b) increasing coordination; c) decreasing the length of covalent bonds and the size of anions; and d) in an extreme regime, moving electrons off atoms and generating new modes of correlation. Examples of the startling chemistry and physics that emerge under such extreme conditions will alternate in this account with qualitative chemical ideas about the bonding involved.

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1. The Extreme Landscape of High Pressure

Pressure and temperature influence all properties of a chemical system. And determine the fate of a chemical reaction. Gases—and phase and chemical equilibria involving gaseous reagents—are particularly sensitive to external pressure. Liquids and solids are much less compressible than gases, though our intuition here is constrained by our everyday experience of pressure (or impact) up to 100 atm. Even higher pressure does not seem to have much effect on matter. A chemistry student, who prepares a standard KBr pellet for an IR spectroscopic measurement (using a manual press) actually applies about 10000 atm to the finely ground material. Yet no major change in the physicochemical properties of the squeezed substance is observed, except for its consolidation into a more or less uniform pellet. The substances in the pellet were just subjected to a pressure of about 1 GPa (10000 bar = 9869 atm = 145038 psi = 1 GPa).

Things change much when one puts on a squeeze of 100 or even 500 GPa to chemical elements or compounds.[1] Under such harsh conditions, the free-energy change of the system (due to the pV term in the Gibbs free energy $G = E + pV - TS$) may reach 10 eV per two atoms,[2] exceeding the bond energy of *any* chemical bond in the 1-atm world. Clearly, in the multimegabar range, new chemical bonds may be created and existing ones severely deformed (usually compressed, but as we will see, occasionally elongated, for a while).

And so they are. For example, an "atomic crystal" of xenon (which melts at −112 °C at 1 atm) turns into a very compact and high-melting ($T_m \approx 3000$ °C!) solid at a mere 50 GPa.[3] Clearly, new and strong Xe–Xe bonds appear (yes, why not call them bonds, even when they may be quite different from the bonds of ambient conditions that we think we know well), and they keep the solid's framework intact even at very high temperatures. We will soon see still more striking physics and chemistry at high pressure.

A pressure of 200 GPa typically leads to a reduction of the volume of a solid by a factor of 1.5–5,[4] which corresponds to a shrinking of the distances along any one dimension (if isotropic) by a factor of around 1.1–1.7. These are huge changes. Is there a place for chemical thinking in this world? Physicists, who have long been active in the study of matter under such extreme conditions, are unlikely to make much

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room for the chemical imagination in matter under such extreme conditions. Yet chemists, with and without the help of detailed quantum-mechanical calculations, have developed effective, productive ways (not one, but many) of thinking about what holds atoms together. The strength of these ideas is precisely in their qualitative nature.

We intend to show that simple ideas of chemical bonding, albeit affected by the extreme conditions, serve as a useful framework for understanding structure and reactivity under high pressure. Or, to put it another way, that a *chemical intuition* may be developed for thinking about matter in the ultrahigh-pressure regime.

In this paper, we will alternate discussions of qualitative ideas of bonding under high pressure with accounts of the startling chemistry and physics that is revealed under these conditions. Ours is not an exhaustive or critical review;[5,6] we mean to illustrate the fascinating phenomena observed with selected examples, to identify structural and electronic regularities, and to try, in a qualitative way, to provide rationales for these.[7] These explanations will of necessity be tentative and speculative.

2. A Hierarchy of Responses to Pressure in Crystals

From many experimental and theoretical studies, a fairly obvious perspective emerges on the factors determining geometrical changes in response to the squeezing of an ambient-pressure molecular solid.

We see four regimes, each with its own length/energy scales, in order of increasing energy:

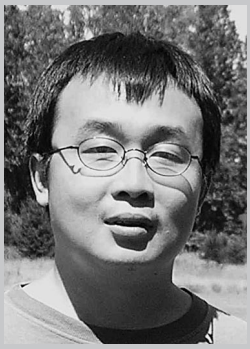
- Penetrating the repulsive region of intermolecular potentials;
- Increasing the coordination at main-group and transition-metal atoms;
- Decreasing the length of covalent bonds and the size of anions;
- A new world of electrons moving off their atoms and new modes of correlation.

No doubt these regimes overlap. Let's look at them, in turn, to see what the new rules of the game are.

3. Squeezing Out van der Waals Space

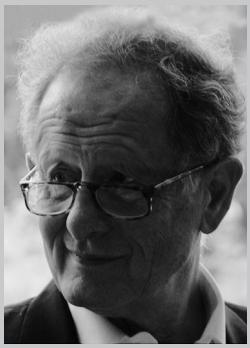
Compressing *molecular crystals* to modest pressure (less than 10 GPa) may be spectacular in terms of the large volume decrease that occurs at the early stages of squeezing—the "van der Waals space" is most easily violated. Figure 1 shows an example from a theoretical examination of silane (SiH_4) under pressure.[8] One of the 13 structures considered in the study begins at ambient pressure as a molecular solid consisting of tetrahedral SiH_4 units, with $Z=1$ in space group $I\bar{4}3m$. In Figure 1, the evolution of the shortest

Wojciech Grochala was born in Warsaw, Poland in 1972. His chemical education and scientific carrier are linked to the University of Warsaw, where he now heads the Laboratory of Technology of Novel Functional Materials. He also studied with Roald Hoffmann (Ithaca) and Peter P. Edwards (Birmingham). The research of his team is centered around novel materials (superconductors, materials for hydrogen storage, molecular memory carriers, and catalysts) and phenomena (high-pressure phenomena, unprecedented high oxidation states of transition elements, and electromerism).



Ji Feng was born in Sichuan Province, China in 1977. He received his B.S. (2000) and M.S. (2003) in chemical engineering from the National University of Singapore. His M.S. thesis work was on the synthesis of nanostructured materials. Propelled by his interest in the chemistry of solids, he became a chemistry graduate student at Cornell University in 2003. He works with Prof. Roald Hoffmann and Prof. Neil W. Ashcroft on the quantum chemistry of crystalline matter under extreme pressures.

Roald Hoffmann has been intrigued by bonding in molecules since his last year at Columbia College, where he was inspired by courses with George Fraenkel and Ron Breslow. His one experimental excursus in graduate school was actually a high-pressure synthesis of a porphyrin that went awry, messing up a brand-new laboratory. He feels that with his interest in building bridges between chemistry and physics he has made chemists less afraid of the language of solid-state physics. As for another aim—to convince physicists that a chemical intuition is of value—the best thing that can be said is that he has not yet given up. (Photo: Maciek Zienkewicz)



Neil Ashcroft was born in London, England shortly before World War II and emigrated to New Zealand in 1947. His first degrees, in physics and mathematics, were obtained from the University of New Zealand; his Ph.D., in theoretical condensed-matter physics, was obtained at the Cavendish Laboratory, Cambridge in 1964 (with Dr. J. M. Ziman). After a postdoctoral appointment at the University of Chicago, he moved to Cornell University, where after four decades he is presently Horace White Professor of Physics, Emeritus. His research interests lie in the theory of many-particle systems, and include the study of electronic and structural order in systems where density can be systematically increased by both static and dynamic means.

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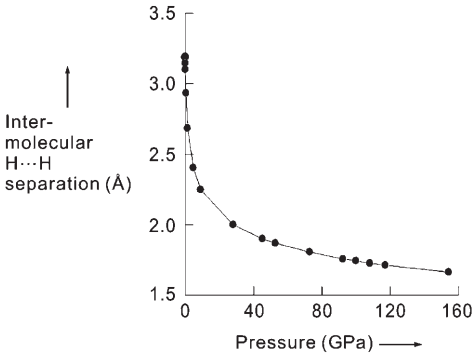

Figure 1. The evolution of the shortest intermolecular H···H separation with pressure in one hypothetical structure for SiH_4. Note the rapid diminution in the H···H separation as the pressure increases to 10 GPa.

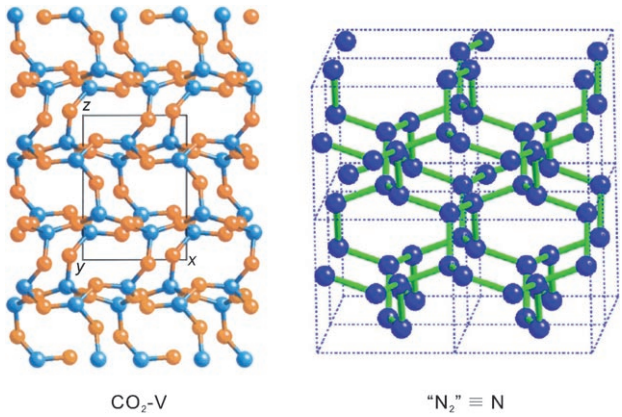

Figure 2. Crystal structures of polymerized CO_2 (phase V; C blue, O orange) and N_2.

intermolecular H···H separation in this structure is plotted as a function of pressure. Note the rapid decrease at low pressure, followed by a slower diminution.

Many questions remain in this regime. With the natural emphasis on the attractive region of intermolecular potentials, which determine phase transitions, too little attention has been paid to the repulsive part of such potentials. A hard-sphere argument doesn't get you far in thinking about the effects of pressure—under high pressure, all walls soften. The question is how much. For instance, what does it cost in energy to reduce an H···H distance in an H_2···H_2 dimer to, say, 1.5 Å? The question is not simple, for we are dealing with "living" matter—the molecules or ions that we think are doing the pressing in the solid state are themselves compressed.

The behavior we observe in the case of silane will be a feature of all molecular crystals under pressure. Let's call it a rough rule: **A) Van der Waals space is most easily compressed.**

Still, not much that is really interesting (for a chemist) occurs in the initial stages of squeezing. But once the intermolecular interactions become stiff enough, the pV term starts working "against" genuine chemical bonds, and the electron-density rearrangement becomes substantial. A typical sequence of events is that atoms increase their coordination, when it is not prohibited by excessive energy barriers. Eventually, the system may undergo a one-, two-, or three-dimensional polymerization, that is, form a nonmolecular, extended phase.[9] Increasing coordination is an obvious way to adapt to higher density.

Let's look at some examples of the spectacular and unusual structural chemistry that develops, and follow that with a qualitative analysis of the underlying bonding.

4. Coordination Alchemy

Squeezing the toughest chemical bonds (those formed by Period 2 elements and by hydrogen) leads to some incredible chemistry. Consider CO_2 and N_2 (Figure 2), which are both thermodynamic sinks and yet unsaturated. That unsaturation is pretty easily violated at high pressure. The linear CO_2 molecule is known to polymerize into an extended solid (phase V; at greater than 35 GPa and 1800 K) that, though the exact structure is unknown, apparently resembles one of the polymorphs of SiO_2.[10] The local coordination of the carbon atoms is close to tetrahedral in phase V. Even N_2, which contains the strongest homonuclear bond, forms a polymer when sufficiently compressed (at greater than 110 GPa and 2000 K).[11] In this new phase, each nitrogen atom is three-coordinate in a pyramidal geometry, as in the ammonia molecule or in the extended structures of the Group 15 elements.

Note that while new bonds are formed in these polymerizations, other bonds are broken. But these are multiple bonds, which—strong as they are—are weaker on a per-bond basis than the underlying σ bonds. Breaking π bonds does not cause much expansion. Forming further new bonds, however, definitely "compactifies". In this world pV rules!

Even those electron-rich molecules which do not have π bonds, but feature "unshared" lone electron pairs, find themselves engaging these unshared pairs in intermolecular bonding at high pressure. H_2O and S_8 provide good examples. When compressed above 60 GPa, water forms "ice X" (Figure 3).[12,13] In this phase, which consists of interpenetrating diamond networks, one can no longer identify intra-

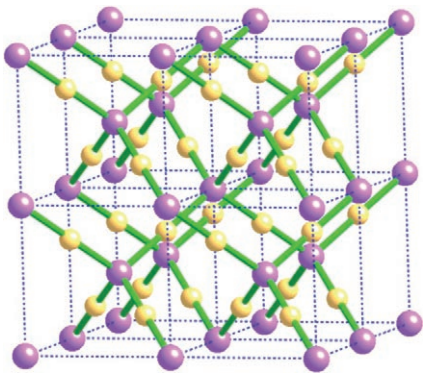

Figure 3. Crystal structure of H_2O (ice X; H yellow, O violet).

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molecular O–H bonds and intermolecular O···H "hydrogen bonds"; all the O–H bonds are now equal in length. Every O–H–O bridge is a symmetrical, strong electron-rich three-center bond. The molecular integrity of the water molecule has completely disappeared.

Elemental sulfur provides another example, now of trading lone pairs for novel σ bonds. At ambient pressure, sulfur exists as a molecular phase featuring classical S_8 crowns (phase I; Figure 4). The shortest intercrown nonbonded S···S

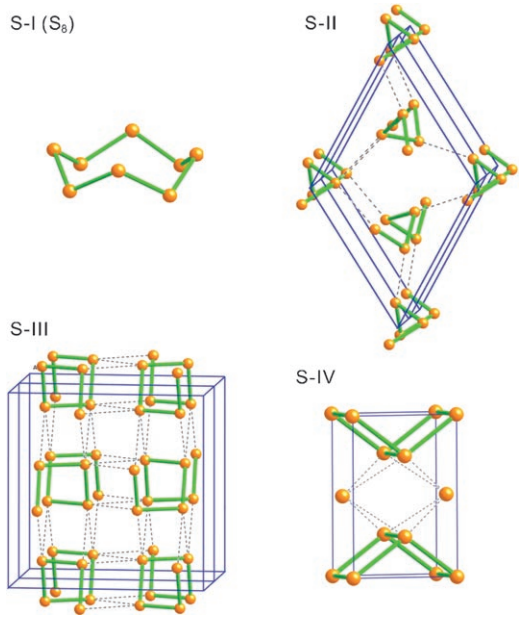

Figure 4. Crystal structures of sulfur at various pressures and temperatures (phases I, II, III, and IV). Note that the structure of S-IV has not been completely refined; the *y* fractional coordinate of S is not determined, and we set it arbitrarily. Primary bonds are shown as green rods, and secondary interactions as dashed lines.

separations are 3.37 and 3.50 Å.[14] Upon progressive squeezing, sulfur first turns into a one-dimensional polymer that consists of helical chains with three atoms per turn (phase II; at greater than 1.5 GPa, on heating).[15] In this structure, the sulfur atoms form two short bonds (2.025 Å), in addition to weak S···S bonding interactions of 3.18 Å and longer.

As the pressure increases above 36 GPa (at 300 K), phase II transforms into phase III. This new allotrope shows helices again, now with a fourfold screw axis. Each sulfur atom makes two short bonds (2.09 Å) at an angle of 101°; there are four secondary contacts of 3.02 Å.

The secondary interactions here make chemical sense—they are reminiscent of many such interactions in the crystal structures of the elements E of Groups 14–17 at 1 atm.[16] One can think about a continuum of donor–acceptor interactions (with a lone pair on E as the donor and the σ* level of a homoatomic E–E or heteroatomic E–X bond as the acceptor) that merges into hypervalence. The longer primary bond in S-III (relative to that in S-II) is coupled with shorter nonbonded contacts. More on this below.

The subsequently formed phase IV (body-centered orthorhombic; at greater than 83 GPa, 300 K), which contains (2 + 2 + 4)- and (2 + 4 + 4)-coordinate sulfur atoms in puckered layers, is metallic (and superconducting[17]). It has gone a long way from two-coordination. The last phase transition found experimentally (so far) occurs above 160 GPa and leads to hexagonal phase V. The ultimate transformations to the simple cubic phase VI[18] and then to the body-centered cubic (bcc) phase VII, with its eight-coordinate sulfur atoms,[19] have been predicted to occur in the neighborhood of (as yet unreached) 285 and 550 GPa, respectively.

Analogies between high-pressure phases of light elements and normal-pressure phases of their heavier congeners are quite general.[20] In the particular example here, phase II of sulfur closely resembles phases of selenium and tellurium found at ambient pressure, while phase III of sulfur is similar to the high-pressure phase Se-VII, and phase IV of sulfur is analogous to the high-pressure phases Se-IV and Te-III. Finally, phase V of sulfur (which is isostructural to Se-V and Te-IV) is also adopted by β-Po.

In an insightful paper, Prewitt and Downs formulated a set of rules of thumb for structural changes at high pressure.[21] These rules are a summary of an immense body of crystal-lochemical and mineralogical experience and are, in turn, inspired by Pauling's well-known crystal-chemistry rules.[22] Two of Prewitt and Downs' rules of thumb are: "4. Increasing pressure increases coordination number" and "9. Elements behave at high pressure like the elements below them in the periodic table at lower pressures." The quasialchemical transmutations of CO_2 (into an SiO_2 structure) and of N_2 (into an allotrope resembling the elemental phosphorus structures), as well as the mutations in the coordination of sulfur allotropes under pressure, are all in accord with these rules. So are many other systems.[23]

If we look at chemistry broadly, it is clear that the really striking ambient-pressure structural dichotomy is between the elements of Period 2 (for example, carbon, nitrogen, and oxygen) and those of the lower Periods. And it is clear that recent high-pressure chemistry has overcome this differential. We think that Prewitt and Downs' rules are quite correct; another way to summarize them is in a rough rule: **B) Ionic and covalent structures, be they molecular or extended, respond to pressure by increasing coordination.**

In this Review, we will extend the rules of Prewitt and Downs (as well as the regularities and strategies noted by Goodenough, Kafalas, and Longho in a perceptive analysis of structural and electronic change under pressure[24]) to the realm of covalently bonded and molecular structures. And we will make a connection to the underlying quantum mechanics and molecular orbital (MO) theory. This we begin next.

5. The Chemical Bond under Pressure

Why should Prewitt and Downs' 4th and 9th rules, or our equivalent rule B, hold? Why should small atoms subjected to high pressure rebond so to resemble their heavier homologues? One might, rather, think that compressing large atoms and forcing them to reduce their atomic volume should make the heavier atoms resemble the lighter ones. Yet essentially the inverse is observed!

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Let us step back and look qualitatively at what pressure might do to the chemical bond.

Qualitatively, the formation of a chemical bond between two (or more) nuclei may be thought of as a way to decrease the internuclear repulsion. Part of the electron density moves from the isolated atoms towards the region between them. We term this increased (shared) electron density a bond.[25] The value of an equilibrium bond length, thus, comes from a compromise between internuclear repulsion, interelectron repulsion,[26] the stabilizing (attractive) electron–nuclear interaction,[27] and kinetic energy.

The above description, along with its implications, is impressive only in its naïveté.[28] As Mulliken said, "The chemical bond is not as simple as we think." But what a productive oversimplification, one that has led to the cornucopia of molecules and extended structures before us …

A further problem we must face at the outset is the ambiguity of the various measures of bond strength, especially when pressure is applied. With some pretty well-understood exceptions (for example, the $^{1,3}\Sigma_u^+$ excited states of C_2, which have an equilibrium bond length shorter than that of the ground state[29]), there is a triple correlation of increasing bond-dissociation energy with decreasing internuclear separation and increasing force constant (Badger's rule). But the bonds of interest to us are squeezed; pV work has been done on them. It's not obvious how to define a bond-dissociation energy under pressure. Still, the distance and force-constant criteria remain and, in our opinion, are good indicators of bonding strength.[30]

When external pressure is applied and the nuclei in a molecule are brought closer to one another, the internuclear repulsion increases. The electron density must adapt to this new situation—it does so such that *more density moves into the internuclear region* (Figure 5).[31]

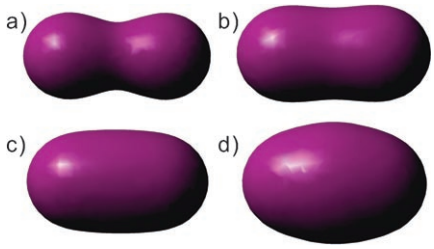

Figure 5. Total electron density in an N_2 molecule (density isovalue: 0.2 e Å^{-3}) for an N–N distance of a) 1.3 Å (an elongated bond), b) 1.096 Å (the computed equilibrium bond length), c) 0.9 Å, or d) 0.7 Å (a significantly compressed bond).

One way to think about this is within the one-electron MO picture of bonding. Consider, for example, a typical bonding MO of a diatomic homonuclear molecule (spatial part): $\Psi = c_1\phi_1 + c_2\phi_2$ with $c_1 = c_2 = 1/\sqrt{2 + 2S_{12}}$, where S_{12} is the overlap between the basis orbitals ϕ_1 and ϕ_2. The electron density for one electron in this MO is $|\Psi|^2 = c_1^2 + c_2^2 + 2c_1c_2S_{12}$. The off-site term $2c_1c_2S_{12}$ is a rough measure of the covalent bonding, that is, the shared electron density.[32] As S_{12} increases, the coefficients c_1 and c_2 decrease, and the off-site term $2c_1c_2S_{12}$ rises at the expense of the two on-site terms c_1^2 and c_2^2.

A chemical bond often shortens on compression. In the process, it becomes *more covalent*. Prewitt and Downs come to the same conclusions in their rule: "3. As a given bond compresses it becomes more covalent."[33] As we will see soon, the decrease in bond distance upon squeezing in the moderate-pressure regime occurs only in the somewhat artificial situation when there are no external bonds being formed.

Applying a "short bond = strong bond" paradigm, a bond should also be *strengthened* under pressure. This effect is also seen in the usual increase of the force constant for bond stretching; that is, *phonons stiffen* as the pressure is elevated. Another way to think about this is that external squeezing trims off the anharmonicity on the long-distance side of a molecular potential.

Exceptions are occasionally found to the strengthening of bonds under pressure, as in the case of the symmetrization of hydrogen bonds. This symmetrization may be associated with the movement of an O–H vibration to lower frequency. In the important case of H_2,[34] as pressure is applied, the characteristic stretching normal mode (vibron) first increases (the effect of direct squeezing on the bond, we think) and then decreases (on the way to the formation of an extended lattice and the onset of metallization).[35]

6. Four Ways To Think about Increased Coordination

The simplified picture just presented applies to existing *intramolecular* chemical bonds. But it may also be extended to the situation when atoms from other molecules come closer to the central atom under consideration. Internuclear repulsion rises then as well, and the system needs to use the same trick as before to counter the repulsion; part of the electron density now must be relocated to the intermolecular region.

The increased-coordination regime is very chemical. The question is: how difficult (or easy) is it for the central atom E of a molecule EL_n (where L is a "ligand") to allow other atoms, originally bonded exclusively to another molecule, into its coordination sphere? In the 1-atm world, molecules of Period 2 elements are known to resist such "associative" reactions by very large energies. But for compounds of elements of the lower Periods, attaining higher coordination numbers (to a maximum of around nine) is pretty easy. So NH_5 (trigonal bipyramidal or square pyramidal) is not a local minimum on its potential-energy surface,[36] but PH_5 and AsH_5, for example, are. Crystallochemical studies reveal a pretty flat potential-energy surface for the increased ligation of silicon, phosphorus, and sulfur.

Here follow four ways to think about the fascinating and crucial phenomenon of increased coordination under pressure. While we will voice an opinion as to which to us seems useful, we do not prescribe one, and only one, way to look at the problem. Some modes of reasoning may be incommensurate (in Kuhn's sense) with others, but they still may be productive. Chemistry often moves forward in just this way.

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6.1. Chemical Hardness and Polarization

Compounds, be they molecules or solids, usually adopt a nuclear arrangement which favors the maximum chemical hardness of the entire system.[37] The chemical hardness η is related to the ionization potential (IP) and the electron affinity (EA) by $\eta = (\mathrm{IP}-\mathrm{EA})/2$; the hardness corresponds to roughly half of the energy gap between the filled and unfilled levels. While we are cognizant of the dangerous anthropomorphism it harbors, another way of saying this is that the ground state of a chemical system (for example, N_2) attempts to minimize the influence of its own excited states by admixing them into itself and, in the process, pushes the excited states up in energy.[38] From still another perspective, this influence of electronic structure on geometry may be described as a second-order Jahn–Teller distortion.

As the pressure is increased above 1 Mbar, some fairly high-lying (at 1 atm) excited configurations may come into play and mix more significantly into the ground state of the system.[39] The argument is related to one we will return to later in a discussion of metallization: levels spread into bands; as a result, the gap between the filled and unfilled levels is usually diminished.[40] The corresponding excitations are at lower energy under pressure, so they mix to a greater extent into the ground state. The relevant excitations for N_2 are of the $\pi \rightarrow \pi^*$ type; they stretch the N≡N bond, and their involvement is necessary to describe an N_2 unit bonded to other N_2 units, that is, polymerization.

The admixing of excited configurations (and the involvement of virtual atomic orbitals, which are nearly unoccupied at ambient pressure) is a mechanism for hybridization. The Period 2 elements are relatively hard. Compression lowers the excited states, rendering these atoms softer and allowing for rehybridization. As a consequence, the hard and less polarizable atoms start to resemble heavier atoms. They become softer; their electron density is now more versatile and less directional.[41] This is one way of understanding why the structures of the compressed light atoms start to resemble those of their heavier analogues.

6.2. Changes in the Importance of Multiple Bonding

Why is multiple bonding (with its concomitant low coordination) not common for the elements of Period 3 or below? The question is important in describing the distinct trends in ambient-pressure chemistry within the Periodic Table.

Here is an MO argument: the distance of the underlying σ bonds is long for these heavier elements. At that distance, the p–p π overlap, which is necessary for effective multiple bonding, is small. The net π–π* splitting of a hypothetical E= E double bond is small; the π bond is then reactive—towards acids, bases, radicals, and polymerization.

The problem is kinetic, not thermodynamic. P_2, with a nice triple bond, is the most stable diatomic molecule of a Period 3 element. But there are no bottles of P_2—the persistent allotropes of phosphorus at ambient conditions all have single bonds in three-connected structures.

While we think that multiple bonding is important to understanding the difference between the chemistry of the Period 2 elements and that of the heavier elements, it is not clear to us what the effect of pressure is on this bonding type.

6.3. s/p Mixing

A high degree of s/p mixing, as occurs in the Period 2 elements, favors definite coordination geometries (for example, the ubiquitous tetrahedron of octet compounds) and what one might call the "saturation of valence". Higher coordination, especially in electron-rich systems, is actually favored for situations where there is *less* s/p mixing.[42]

All the evidence (at ambient pressure) points to diminished s/p mixing as one goes down a Group. The overlap governs the interaction between the s and p orbitals (through the factor H_{ij}^2 in the perturbation-theoretic expression $\Delta E = H_{ij}^2/(E_i - E_j)$, where H_{ij} is the matrix element of the Hamiltonian and is roughly proportional to S_{ij}, the overlap of the interacting orbitals). As one descends a Group, the s orbitals turn out to be more poorly screened than the p orbitals of the same principal quantum number. The occupied s orbitals are closer to the nucleus (in large part owing to a relativistic effect), and their overlap plays a smaller role in chemical bonding as one goes down a Group.

We have not found a good way to use s/p mixing as an explanation of coordination alchemy under high pressure. In the first instance, compression would seem to increase s/p mixing for the elements of Period 3 and below, pushing systems of these atoms to definite coordination modes with numbers of two, three, or four. This hypothesis is not consistent with the structural evidence, nor does it explain the changes seen in the coordination of the elements of Groups 14–16 under pressure.

6.4. VSEPR

The valence shell electron pair repulsion (VSEPR) model[43] (based on Lewis structures, which are dear to the heart of every chemist) allows qualitative rationalizations and, in some cases, predictions of molecular geometries for a broad range of compounds. In the VSEPR model, one identifies local electron pairs (lone pairs and bonding pairs) and, in the simplest version, approximates them by point electric charges. The minimization of the repulsion of the localized pairs yields the preferred arrangement of ligands around an atomic center.

Within the VSEPR framework, what might one imagine happens at high pressure? As various centers surrounded by substantial electron density are forced closer to one another, the separation between the localized electron pairs, therefore, diminishes. One way to decrease the electron–electron repulsion *within each pair and between the pairs* is to rebond in such a way that the new crystal phase has more bonds around an atom, but less electron density within each bond. Thus, in a very general way, polymerization and an increase in coordination number at high pressure make sense within the

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VSEPR model. Whether anything of predictive value emerges from this viewpoint remains to be seen.

There are two bonding types which we think contribute more than other types to the middle-energy regime under high pressure, where atoms expand their coordination sphere. These are discussed next.

7. Multicenter Bonding as a Way of Increasing Coordination

Be it in $B_{12}H_{12}^{2-}$ or XeF_6, chemists have faced up to the problem of atoms forming more bonds than the number for which there seem to be sufficient electrons or orbitals.[44] The ideas of electron-poor and electron-rich three-center (or multicenter) bonding serve well here. These ideas are familiar to chemists; a brief review is given in Appendix A. As we will show, multicenter bonding really helps us think about the increase in coordination under high pressure.

Closely related to electron-rich three-center bonding is a typical structural feature (often talked about under the rubric of "secondary interactions") found in myriad ambient-pressure crystal structures: a lone pair on one atom "faces" or points at a σ bond in another molecule, at a separation which is less than the van der Waals distance.[16] *Such secondary interactions are rarely repulsive in the elements of Period 3 or below.*

And they are a harbinger of what happens under pressure. These secondary interactions, which shade over into electron-rich three-center bonds, give rise to a critical set of compactifying interactions, leading in many cases to an increase in coordination number beyond the classical values of two, three, or four. To anticipate matters, this effect is at work in the high-pressure sulfur structures we showed, as well as in what happens to the structure of iodine under pressure, or to the structures of the Group 15 elements, especially those of arsenic and antimony, which go simple cubic under pressure.

How can these important secondary interactions be attractive, and what is their relationship to symmetrical three-center bonding? It makes sense to take a donor–acceptor approach to this bonding type. Consider as a prototype the I_3^- ion, formed from I^- and I_2. As the I^- ion approaches the I_2 molecule, there is certainly a repulsive interaction between the p orbital of I^- and the higher-lying lone-pair n orbital of I_2 (Figure 6). But at the same time, there is an attractive donor–acceptor interaction between the p orbital of I^- and the relatively low-lying σ* orbital of I_2. The resulting orbitals can be shown to evolve smoothly into those of the symmetrical three-center bond.

As this picture implies, often there is a balance of bonding forces (attractive and repulsive) in these systems with donor–acceptor/electron-rich three-center bonds. So at ambient pressure, sometimes the I_3^- ion is symmetrical, sometimes not.[45] The barrier to symmetrization (that is, increased coordination at the central iodine atom) cannot be large—in the gas phase, it is zero. A similar set of interactions is available to molecular I_2 under pressure (at a slightly smaller electron count per atom). In general, for the elements of Period 3 and below, an increase in the coordination number

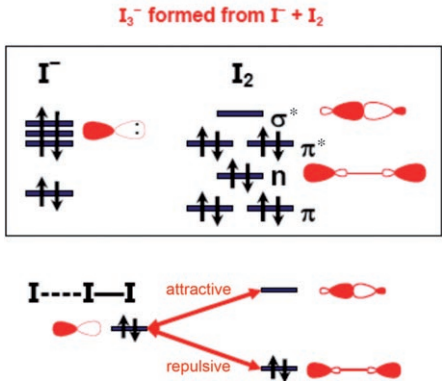

Figure 6. Frontier orbitals for the approach of an I^- ion to an I_2 molecule to form an I_3^- ion. The important orbitals are drawn out in red.

from the norm of one in Group 17 (and for hydrogen), two in Group 16, three in Group 15, or four in Group 14 is facile and involves little cost in energy.

Symmetrical and unsymmetrical alternatives (for the same electron count) are common in a number of ambient-pressure crystal structures. A striking example is the Li_2Sb structure, which features linear Sb^{2-} infinite chains coexisting with Sb_2^{4-} pairs.[46] And there are a multitude of ideal square lattices (and distortions therefrom) in compounds with a valence electron count of five.[47]

The propensity to enter multicenter bonding through both electron-poor and electron-rich schemes is enhanced under pressure, as we proceed to show through several examples.

7.1. Pressure-Induced Electron-Deficient Bonding

Electron-deficient bonding schemes can be used to describe the non-diamond structures of Group 14 elements. And they are one way to account for the Si–H bonding (ignoring H–H and Si–Si interactions, for the moment) in some of the recently (theoretically) explored high-pressure structures for SiH_4.[8,48,49]

Consider, for instance, a relatively low-enthalpy (at high pressure) structure of SiH_4 (in space group $I4_1/a$) suggested by Pickard and Needs, which is shown in Figure 7 (left). Each silicon atom has eight nearest-neighbor hydrogen atoms, pairs of which bridge to four neighboring silicon atoms. The stoichiometry is $SiH_{8/2}$. Each Si–H_2–Si unit uses four electrons (one from each silicon and each hydrogen atom) to bond the four centers in a diborane fashion, as proposed by Pickard and Needs. And there are four such Si–H_2–Si bonding units for each silicon atom.

The problem is that, on the face of it, this bonding scheme requires eight participating orbitals from each silicon atom, but the silicon atom has only four. This situation has been encountered before, and one can resolve it with no great difficulty, by using just the s and p orbitals of the central atom for delocalized bonding. Our structure, similarly, has eight three-center electron-deficient Si–H–Si bonds around any given silicon atom (Figure 7, right).

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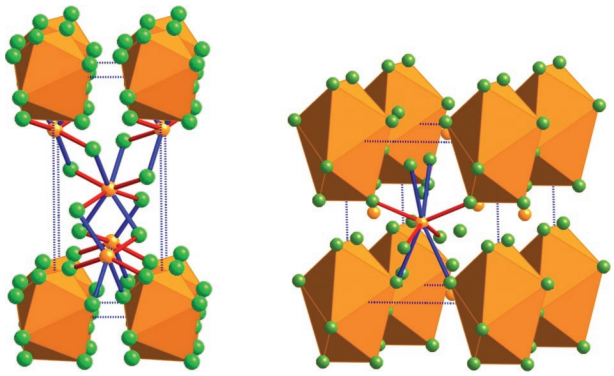

Figure 7. Two low-free-energy structures for SiH_4 under pressure containing eight-coordinate silicon atoms (H green, Si orange). In the structure at the left (due to Pickard and Needs,[48] at 160 GPa), each silicon atom forms four pairs of (diborane-like) hydrogen bridges to four silicon atoms. In the structure at the right (144 GPa),[8] each silicon atom is involved in eight (4+4) Si–H–Si bridges to eight different silicon atoms. The two structures seem quite different, but in each the environment of the silicon atoms—a deltahedron (orange) of hydrogen atoms, comprising one squashed (red rods) and one elongated (blue rods) tetrahedron—is remarkably similar.

In general, if one is starting with a saturated molecule, a methane analogue, and one subjects it to high pressure, the only way that one can move to higher coordination (as one must eventually) is through electron-deficient multicenter bonding.

7.2. Electron-Rich Multicenter Bonding under Pressure

The effect of pressure on an electron-rich three-center system may be gleaned from a selection of structures with $F^-\cdots Sb\cdots F^-$ fragments from the Cambridge Structural Database (CSD).[50] If $R1$ is one $F^-\cdots Sb$ distance, and $R2$ the other, then $R1+R2$ gives an idea of the total "size" of the three-center system (to be thought of as more or less inversely dependent on the pressure), and $R1-R2$ measures the asymmetry. Figure 8 shows a plot of $R1-R2$ versus $R1+R2$ for a selection of structures. Note the large clump of

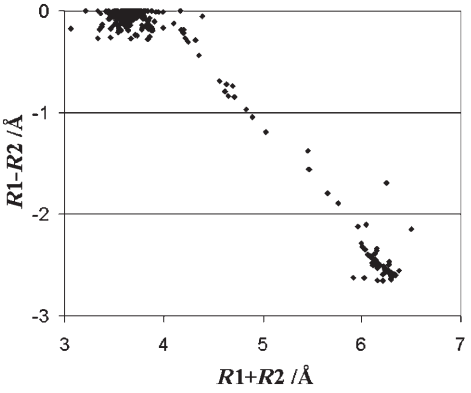

Figure 8. Plot of $R1-R2$ versus $R1+R2$ for a large number of hypervalent $F^-\cdots Sb\cdots F^-$ moieties from the CSD, where $R1$ is the shorter and $R2$ the longer of the two $F^-\cdots Sb$ contacts.

structures that are close to symmetric at small $R1+R2$ values and the prevalence of asymmetrization only at large $R1+R2$ values. The more space one "leaves" for the $F^-\cdots Sb\cdots F^-$ system, the more asymmetric it becomes. The analog computer of the experimental structures (no calculations here!) clearly suggests that symmetrization—and with it increased coordination—is favored as the pressure is increased. A similar picture applies to a huge variety of hypervalent fragments in the CSD.

In summary, we come to a rough rule: **C) Increased coordination is achieved relatively easily through donor–acceptor bonding, which shades over into multicenter bonding. Such multicenter bonding, electron-rich or electron-poor, is a mechanism for compactification (hence, a response to elevated pressure) for elements across the Periodic Table.**

Two final comments: First, the theoretical part of the above discussion has not invoked d orbitals for the main-group elements. The post-Pauling consensus is that higher angular-momentum functions (for example, 3d orbitals for sulfur) may admix, but they serve primarily to improve the basis set, and their participation is not essential[51]—at ambient pressure. However, as we will see in Section 15, there are well-established cases where high pressure brings about real occupation of virtual (at 1 atm) orbitals. And where even a small occupation of d orbitals greatly influences selected observables of pressurized systems. So the question of d-orbital participation will have to be reopened at high pressure.

At very high pressure, coordination numbers will perforce be very high, beyond eight. It's obvious that the coordination number, which is not all that easy to define at ambient pressure, is harder still to quantify at extreme pressure. Everything is getting closer together, and all one can do is to look both at the relative nearest-neighbor distances and at the absolute values of the distances.

With respect to the importance of multicenter bonding types, this issue brings us to a second point: really high n-fold coordination, even for elements on the right side of the Periodic Table—the home of the electron-rich—must involve delocalized bonding based on four central-atom orbitals (for a main-group element and not using d orbitals) and n "ligand" orbitals. It is possible to construct bonding schemes for pretty much all such situations.[52] The resulting bonding situation is by necessity electron-deficient for such high coordination. Thus, electron-deficient and electron-rich considerations merge into one multicenter bonding scheme.

8. A Numerical Experiment: Pushing Hard on N_2

Our artificial division of various squeezing regimes obviously cannot be precise. In an attempt to conceptually order things, we have separated processes which, in fact, occur simultaneously (but with different consequences for the total energy) as pressure is applied to condensed matter. As far as molecular crystals are concerned—and we will soon move beyond these—gradual penetration turns on incipient secondary interactions. Upon subsequent squeezing, these "weak bonds" turn into stronger ones. The coordination number

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increases, and the system polymerizes. Meanwhile, the "old" covalent bonds also get compressed.

Sometimes it's easier to do things in a computer. The various regimes of squeezing are illustrated by a numerical experiment[31] on a hypothetical N_2 trimer, $(N_2)_3$. Two N_2 molecules (with the bond length kept at 1.096 Å) are pushed towards a third, central N_2 molecule (for which the bond length R is allowed to vary freely as the optimization proceeds; Figure 9a). The N≡N···N angle is arbitrarily fixed at 109.47°. Figure 9b and c plot the total energy of the system and the optimized central distance R.

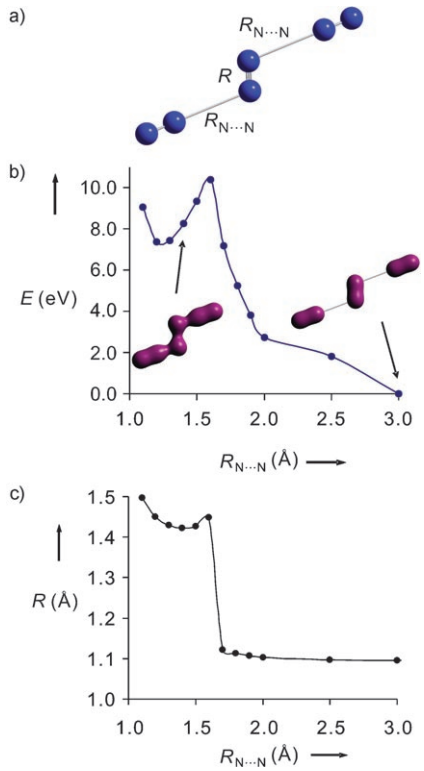

Figure 9. Results of a computer experiment on a hypothetical $(N_2)_3$ molecule.[31] a) The internal coordinate system. b) Plot of the total energy E as a function of the distance $R_{N\cdots N}$ between the central and pressing N_2 units. The total electron density in the $(N_2)_3$ molecule (density isovalue: 0.2 e Å^{-3}) is shown for the $R_{N\cdots N}$ distances of 3.0 and 1.4 Å. c) Plot of the intramolecular separation R for the central N_2 unit, the one being pushed upon, as a function of $R_{N\cdots N}$.

As the distance $R_{N\cdots N}$ between the central and the pressing N_2 molecules decreases, significant reorganizations of the electronic structure take place. The total energy of the system at first rises very slowly, until an $R_{N\cdots N}$ value of about 2 Å is reached. This region mostly corresponds to the first regime (compression of the van der Waals space). But there are also attractive interactions at work here, between the "attacking" lone pairs of the outer N_2 units and the π^* orbitals of the central N_2 unit. In the region $1.7 < R_{N\cdots N} < 2.0$ Å, these attractive interactions actually lengthen the central bond somewhat.

Continuing the simulated squeeze, the energy rises very steeply, reaching its highest value at $R_{N\cdots N} = 1.6$ Å, after which the energy decreases again. Along the same itinerary, the central bond length R actually shows a shallow rise from 1.096 (a typical N≡N bond length) to 1.12 Å (at $R_{N\cdots N} = 1.7$ Å), and then jumps to 1.45 Å (a typical N–N single bond length; at $R_{N\cdots N} = 1.6$ Å). The discontinuities we see here, with their energy and distance cusps, are characteristic of "forbidden" reactions,[53] that is, of level crossings along a reaction path. R then decreases for shorter $R_{N\cdots N}$ separations ($1.2 < R_{N\cdots N} < 1.6$ Å), accommodating the new electronic situation.

The last regime, the firm squeezing of a covalent bond in a molecule of a low-Z element, is the highest-energy process. Here it is exemplified by the region of $R_{N\cdots N} < 1.2$ Å. At such short N···N separations, two newly formed ("intermolecular") σ bonds, as well as the original ("intramolecular") σ bond of the central N_2 unit, are collectively squeezed. Our calculations just begin to explore this region; we do not go further in because a model in which the distances in the external N_2 units are frozen is not realistic in this pressure regime.

Overall, as the two external N_2 molecules approach the central N_2 molecule upon squeezing, the electron density at the central N≡N bond is significantly decreased, while new electron density builds up in the N···N regions (Figure 9b).

We mentioned above the sudden jumps in energy and distance in this model reaction. This result leads us to our next considerations.

9. Anything To Learn from Orbital-Symmetry Control?

In a way, compression resembles a concerted chemical reaction. Indeed, one of the hallmarks of such a reaction is a negative volume of activation. There is a conceptual opening here, since extreme volume contraction, in one way of thinking, creates high-energy waypoints. Could the electronic discomfort generated then be viewed as progress along a forbidden (in the sense of the ideas of orbital-symmetry control[53]) reaction path? From which the molecules try to escape along various vibrational and rotational degrees of freedom? The apposite language may be that of certain lattice phonons or pseudorotations being activated by pressure.

At this point, it is also appropriate to raise the question of a quiet hope in the high-pressure community—that after static or shock compression, the queer (from a 1-atm-prejudiced viewpoint) high-pressure structures could be returned intact to the ambient world.[54] To put it another way, high pressure might become a synthetic tool, even one of industrial significance.

That this scenario might happen is, of course, encouraged by the story of diamond—made by high pressure, geochemically or in the laboratory, and indeed kinetically very, very persistent, despite being metastable at 1 atm. Could one possibly hope for the same in the case of the unusual high-pressure polymorphs, for instance, of N_2 or CO_2? We doubt it can be done for nitrogen.[55] How much phosphorus one would have to admix with nitrogen to allow ambient-pressure recovery of singly bonded allotropes remains to be studied.[56]

The problem has been broached in the literature, in a number of guises.[57] We note especially the chemically

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oriented review of Schettino and Bini, and their work on selectivity in butadiene reactions under pressure.[58] Many of the phase transformations to radically new polymorphs are accomplished at high temperature (as well as high pressure). Large activation barriers have been overcome. If the new polymorph is quite unstable thermodynamically (at ambient conditions), and if the reaction that re-forms the polymorph that is stable at ambient pressure is allowed (especially if it involves gaseous products), it is unlikely that the high-pressure polymorph will survive. But when all pathways of return to the more stable structure are symmetry-forbidden, involving level crossings, the metastable isomer may survive. Perhaps one could formulate a rough rule: **D) Orbital-symmetry considerations will affect the chance that a high-pressure product survives return to metastability in the ambient-pressure world.**

A complication we have avoided previously needs to be raised. A number of chemical reactions under high pressure involve disproportionations and the escape of one product. An example is the transformation of N_2O to $[NO]^+[NO_3]^-$, which must be accompanied by formation of N_2.[59] An interesting case is CO, which transforms, photochemically above 3.2 GPa and thermally above 3 GPa (with heating), to a polymer that survives return to ambient conditions, with some loss of CO_2.[60] The structure of the polymer—which seems to contain five-membered lactone rings and conjugated C=C chains—is not simple.

At this point, let us leave molecular solids and move to a discussion of another bonding extreme, the ionic one, under pressure.

10. The Differential Compression of Ionic Lattices

The long standing—and continuing—interest in pressure-induced phase transformations in "simple" ionic halides has provided us with a broad spectrum of experimental and theoretical data on ionic solids under pressure. So has the mineralogy of the interior of the earth. It turns out that the MX compounds (M = Na, K, Rb; X = F, Cl, Br, I) change from the ambient-pressure NaCl (B1) structure to the CsCl (B2) structure at high pressure.[61,62] The coordination of M^I is sixfold (octahedral) in the B1 structure, while it is eightfold (cubic) in the B2 structure.

That the lighter alkali metals again tend to resemble the heavier one, cesium, at high pressure might be considered as the work of Prewitt and Downs' 4th and 9th rules. But remarkably, the B1–B2 transition occurs at a similar pressure, p_T, for all the halides of a given cation. The transition pressure decreases sharply with the size of the cation, as exemplified by halides of rubidium ($p_T \approx 0.3$–0.5 GPa), potassium ($p_T \approx 1.9$–3.5 GPa), sodium ($p_T \approx 27$–32 GPa), and lithium ($p_T >$ 100 GPa[63]). The very modest dependence of the transition pressure on the kind of anion points to the obvious importance of the cation size—as we know it from the 1-atm world—for achieving eightfold coordination.[64]

While being aware of the intriguing proposition of O'Keeffe and Hyde that one might refocus on the crystallochemical role of cation–cation interactions,[65] we are following here a classical point of view on the determinants of crystal structure.

Indeed, anions are orders of magnitude more polarizable than cations,[66] and they are also much more compressible.[67,68] Therefore, as squeezing progresses, essentially it is the size of the anions which is diminished. This effect allows for more efficient packing of the anions around a given cation. And for the electron density from internuclear regions (sixfold coordination) to be utilized for extra bonding (eightfold coordination).

We are now in the realm of mineral structures important for geochemistry. Some of Prewitt and Downs' rules address such structures explicitly: "5. The oxygen atom is more compressible than the cations" and "7. O–O packing interactions are important." Again trying to cover both the covalent and the ionic realms, we think one can summarize a lot of knowledge in a rough rule: **E) In ionic crystals, the anions are more compressible than the cations; therefore, the coordination number (especially that of the cations) increases at high pressure**.

Of course, it should be easier to pack eight small F^- anions than eight large I^- anions around, say, a K^I cation. However, the I^- anion is also more compressible than F^-. It seems that both trends nearly cancel out, thus, yielding similar transition pressures for KF and KI.

There are many interesting manifestations of the decrease of the anion size under high pressure. These are exemplified by phase transitions observed for CaO,[69] CdO,[70] and the related compounds BeX (X = Se, Te),[71] BAs,[72] CsH,[73] Si_3N_4,[74] Ge_3N_4,[75] P_3N_5.[76] One might be surprised to see Cs^I going 11-coordinate, Sc^{III} going into a cubic site,[77] or small Be^{II} or B^{III} going six-coordinate while surrounded by Te^{2-} or As^{3-} anions of appreciable size.[78]

Applying rule E to an environment of F^- anions, we may expect octahedral Sn^{IV}, Pb^{IV}, Pa^{V}, or U^{VI} cations to become eight-coordinate,[79] while larger cations (such as Zr^{IV}, Hf^{IV}, Ce^{IV}, or Th^{IV}) might go to 10- or even 12-coordinate environments. But this is just the beginning; the spectrum of substances studied so far is really narrow, and encompasses selected elements and a small range of binary and ternary compounds (predominantly oxides). Much more is to come.[80–82]

11. Metallization under Pressure

The calculations on SiH_4 and GeH_4, predict that the tetrahydrides of the heavier Group 14 elements should be metallized at moderate pressure.[8,48,49] It is time to address a central issue in high-pressure studies: the metallization of semiconductors and insulators.

The metallization of semiconductors, or even insulators, is not new. As early as 1935, Bernal (cited by Wigner and Huntington[83]) noted what we might call a rough rule: **F) All materials become metallic under sufficiently high pressure**.

But why should something like this happen? The answer can be provided from at least two perspectives. The first one is simple: compression leads to greater overlap and, thus, to greater interaction among both filled and unfilled MOs.

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Consider, for example, a hypothetical simple cubic lattice of krypton atoms. A chemist will describe its electronic configuration as $[Ar]3d^{10}4s^24p^65s^05p^0$; its valence 4p electrons are well-separated from the unoccupied 5s orbitals (by about 8 eV). At ambient pressure, krypton atoms—enjoying their octet configuration—interact only very weakly with each other. A large separation in energy between the 4p and the 5s manifolds assures that the polarizability of krypton is small[84,85] and that the dispersive interactions are ultimately weak. Figure 10 shows the outcome of a model calculation.[86]

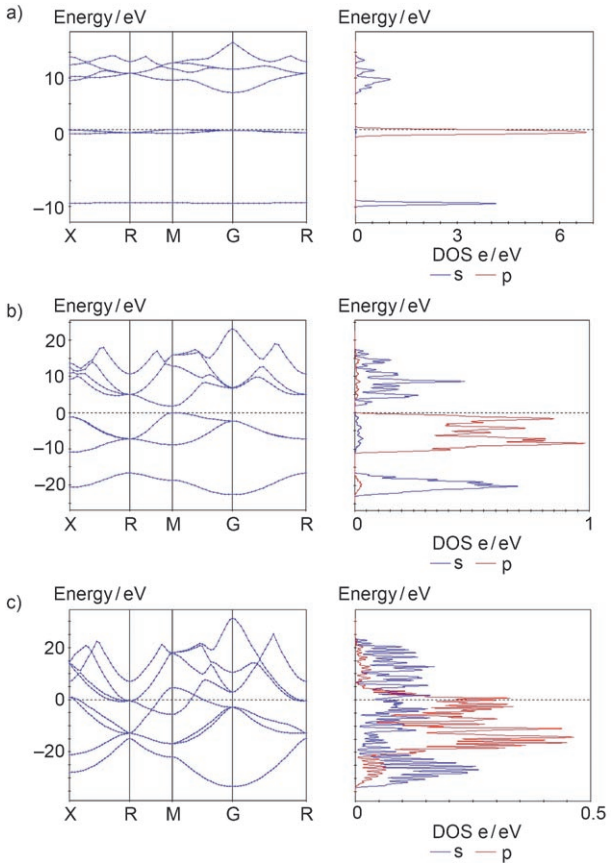

Figure 10. Illustration of the pressure-induced band-gap closure for a model system, a simple cubic crystal of krypton atoms. Band structures (left) and density of states (DOS) plots (right) a) for $a = 4.04$ Å at 0 GPa (the band gap is 8 eV), b) for $a = 2.60$ Å at 100 GPa (the direct band gap is 3 eV), and c) for $a = 2.11$ Å at 500 GPa (the band gap is now closed). The contribution to the DOS of the s orbitals is in blue, and that of the p orbitals in red. The dashed lines indicate the Fermi level.

At a Kr···Kr separation of 4.04 Å (a typical length for a van der Waals contact), the electronic bands formed from 4p orbitals are computed to be quite narrow, with a dispersion of about 2 eV (Figure 10a). The bands formed from the more diffuse virtual 5s and 5p orbitals are much wider, their dispersion being about 10 eV.

When pressure is applied to our model crystal, and the krypton atoms are brought closer to one another, their occupied and unoccupied atomic orbitals start interacting more strongly. The corresponding bands spread progressively with the applied pressure, and the band width grows steadily. The width of the 5s/5p band increases to 20 eV at 100 GPa, while the width of the 4p band reaches 10 eV at this pressure (Figure 10b). If this trend continues, then at a sufficiently large pressure, the gap between the two bands should close through band crossing (Figure 10c). Thus, in theory at least, the localized valence electrons of krypton, xenon, or radon should become delocalized at some point.[87]

No one has yet seen this for krypton. But the heaviest and the most polarizable among nonradioactive noble gases, xenon, has been forced to surrender its nobility, by forming a hexagonal close-packed (hcp) lattice at 70–90 GPa and then undergoing metallization at a much higher pressure (132–150 GPa).[88] Its isoelectronic ionic analogues CsI and BaTe have also been metallized at comparable pressures of 115[89] and 200 GPa,[90] respectively. Indeed, beyond a certain compression, the equations of state of CsI and xenon are well nigh indistinguishable.[91] CsI is a nice example of an ionic halide in which the large, polarizable lone pairs of the I^- ion achieve metallization through band overlap with diffuse Cs^I states.

We note that over a range of intermediate pressures band-gap diminution is not universal. For classical semiconductors, the direct band gap often increases with pressure over a substantial pressure range.[40,92] And there are indications that in certain metallic structures (for example, those of lithium,[93] and calcium[94]) bands may narrow with pressure.

There is another way to look at metallization: the Goldhammer–Herzfeld criterion for metallization[84] is simply that an insulator or semiconductor is likely to become a metal when the conditions on the density are such that the bulk polarizability diverges; that is, electrons can be ripped of the atoms or molecules with an infinitesimal perturbation. This argument predicts that a material becomes metallic when the value of $f\alpha V_m$ equals unity, where f is a dimensionless crystal-packing factor, α is the static polarizability of the microscopic constituent, and V_m is the volume taken by that constituent. One immediately sees that the key variable here is the density, which can be tailored by modern high-pressure technologies. The Goldhammer–Herzfeld theory works remarkably well for many systems.

In the following section we will see how a change in crystal symmetry can give rise to and/or suppress metallicity.

12. Moving to Higher Symmetry

While human beings fall for symmetry, there is no evidence that nature does. Those A–B–A molecules that are stable, whether they are linear or bent, do have equal A–B distances. But there are just as many dissociated A + B–A systems, which represent the extreme of asymmetrization. The case of I_3^- cited above is a relevant microcosm—there are hundreds of structures, symmetric and asymmetric, of this anion, as it pairs with different cations.

In thinking about symmetry, or departure from it, the Jahn–Teller theorem, in its first- or second-order incarnations, has been immensely useful.[95] The characteristic symmetry operation in the crystalline state is translation; a Jahn–Teller-

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type distortion breaking translational symmetry (and consequently other symmetry) is called a Peierls distortion. A brief introduction to the Peierls distortion is given in Appendix B.

There is a more formal way to express this concept, in the context of one-electron band theory for crystalline solids. In the case that two electronic states (orbitals) at the Fermi level are related by some **k*** vector in reciprocal space (nesting vector), a distortion allows energy stabilization through a coupling of the two crystal orbitals, if the distortion renders **k*** a reciprocal lattice vector.[96] Nearby orbitals that are only approximately degenerate can also contribute to the stabilization upon distortion, through second-order effects.

Interatomic spacing is, in general, reduced under pressure. In a Peierls distortive system, this reduction normally results in an increase in the band dispersion, which in turn leads to an increase in the energy difference between the paired interacting states close to the Fermi level (Figure 11). Thus, the magnitude of the stabilization which may be gained from the Peierls distortion is diminished.

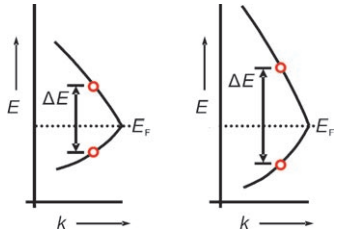

Figure 11. The energy gap ΔE between interacting levels (red circles) near the Fermi level E_F increases with increased band dispersion on going from lower (left) to higher (right) pressure. The term ΔE enters the perturbation expression for the stabilization of the system in the denominator; a large value diminishes the stability gain from a Peierls distortion.

This situation is why distortion, even if it occurs at 1 atm, may be reversed upon compression. Such is the case of, for example, "$CsAu^{II}Cl_3$" (which is known at 1 atm in its cooperatively distorted Jahn–Teller form $Cs_2[Au^{I}Cl_2]$-$[Au^{III}Cl_4]$).[97] A similar reversal of the Peierls distortion should also occur for "$Tl^{II}F_2$" (otherwise described as $Tl^{I}Tl^{III}F_4$),[98] "$Ni^{III}F_3$" ($Ni^{II}Ni^{IV}F_6$), or "$Ga^{II}Cl_2$" ($Ga^{I}Ga^{III}Cl_4$).[99]

In molecular chemistry, we have recognized (rather slowly) that a balance between the rigidity and distortivity of bonds determines the symmetry of some molecules. For example, benzene's π bonds are second-order Jahn–Teller distortive, while the molecule's σ bonds afford rigidity; a benzene molecule does not exhibit bond alternation.[100]

A similar scenario applies to extended metallic solids. The greatest contributions to a Peierls distortion come from states near the Fermi level, where partially filled bands are involved. While the Peierls effect provides a distortive force, other interactions, such as Coulombic repulsion and repulsions incurred in bands below the partially filled band may resist a distortion. For example, the filled σ manifolds in a π-distortive system (for example, a linear system) could be effectively repulsive, because a filled band upon a pairing distortion will break up into a bonding band and an antibonding band. The bonding band will be stabilized compared to the undistorted system, while the antibonding band will be destabilized, to a greater extent. This situation is a classical consequence of overlap, which is called, in the chemical setting, a four-electron repulsion or a Pauli repulsion. Overall, there is an energy penalty from any completely filled band in a pairing motion.

Reduced interatomic spacing also makes the repulsive interactions steeper; that is, there is a larger energy cost for the same amount of distortion. This effect is demonstrated qualitatively in Figure 12, where various state energies are plotted as functions of the generalized distortion coordinate x. A distortion will be realized only when sufficient stabilization can be derived from a Peierls-type perturbation.[101]

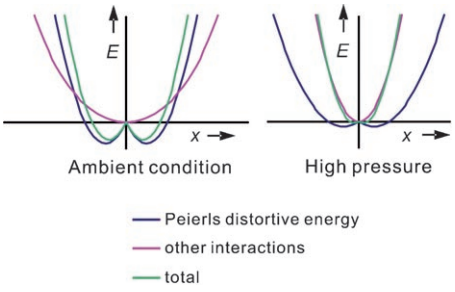

Figure 12. Plots of the energy E components in a distortive process as a function of the generalized distortion coordinate x, at ambient pressure and at high pressure. Note that the energy curves need not be symmetric.

Let's look at a specific high-pressure problem in this context. The ambient-pressure solid iodine crystal is composed of I_2 molecules, pairs of iodine atoms. Experimentally,[102] the structural transformation of I_2 under pressure consists of a continuous dissociation of I_2 molecules, or a lengthening of the I–I bonds. A two-dimensional array of I_2 molecules with a rectangular unit cell dissociates into square nets of iodine atoms. This dissociative process is usually understood in terms of localized interactions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of neighboring I_2 molecules. But as the structure becomes increasingly extended, a delocalized MO picture may be more appropriate. Also, curiously, the iodine crystal is incommensurate for an extended pressure range. An alternative view of the pressurization process based on Peierls distortion, or its reversal, may be useful.[103]

In Figure 13, we show the Fermi surface of a square net of iodine atoms in the metallic state. Two of the nesting vectors,[104] **k*** and **k*′**, can both become reciprocal lattice vectors upon a distortion dictated by **a*** and **b***. This distortion corresponds to what happens in an iodine crystal under ambient conditions.

Pressure then turns on a reversal of the Peierls distortion.[105] The incommensurate character in the structure arises from a continuous and subtle deformation the Fermi surface.

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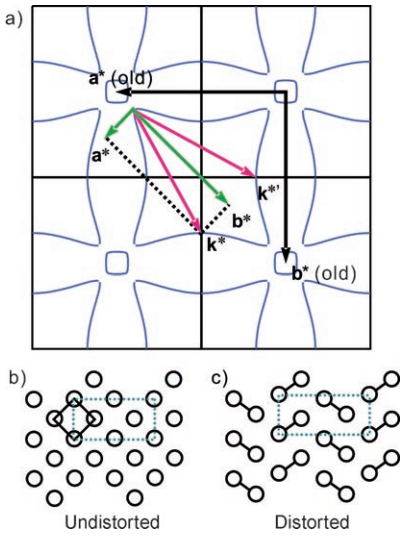

Figure 13. a) Fermi surface (extended-zone scheme; each black box is a first Brillouin zone) of a square net of iodine atoms with a shortest I–I distance of 2.9 Å, based on extended Hückel calculations. The vectors **a*** (old) and **b*** (old) are the primitive reciprocal lattice vectors of the square net. Two possible nesting vectors, **k*** and **k***′, indicate a possible distortion to a rectangular unit cell corresponding to **a*** and **b***. b) The monolayer of iodine atoms before the distortion. The tetragonal unit cell is indicated with solid lines, and the rectangular supercell dictated by the nesting vectors with dashed green lines. c) The experimental (distorted) structure of iodine at 19 GPa,[102] with an I–I bond length of about 2.72 Å.

Our calculation shows that the topology of the Fermi surface of the two dimensional square net of iodine atoms is actually quite robust to compression. Under severe compression, the stabilization of the distortive Peierls energy can no longer compensate for the associated energy cost. The structure will then become symmetric. In the case of iodine, it adopts a monatomic lattice with an odd number of electrons per primitive unit cell, which necessarily leads to metallic character, putting aside the question of possible magnetic ordering.

We come to more of a guide than a rough rule: **G) Thinking about Peierls distortions (their enhancement and suppression) is helpful in understanding symmetrization (or its absence) in solids under high pressure**. While under compression, in general, the stability gain from Peierls distortion is diminished, and steeper repulsive effects favor symmetrization. There are other factors to consider, for example, in good, simple metals. As we discuss below.

13. ... Or Is It Lower?

The other side of the story is no less interesting. Most strikingly, by now there are *many* known high-pressure structures of elements that depart from ambient- or moderate-pressure close-packed structures for denser lower-symmetry alternatives.[106]

The Peierls distortion may be a good way to think about some unusual symmetry-lowering deformations, if one allows oneself to leave the comfortable paradigm of electrons, even if delocalized, that are still associated to atomic cores. A beautiful manifestation of such a phenomenon is to be found in one of the "simple" metals, lithium, which is predicted to undergo an astounding symmetry-breaking pairing under pressure.[87a] And it does just that.

A special Peierls distortion is believed to be involved in this deformation. What happens is that, with increasing pressure, the "inactive", and more or less rigid, filled core state ($1s^2$) of lithium gains importance by occupying a larger fractional volume. A consequence is that exclusionary forces on the valence electrons rise, offering these electrons a smaller and smaller ballroom for their quantum mechanical dance. The result of a greater potential from the core levels is a greater stabilization upon viable Peierls distortion.

In the paired Li_2 state, the lithium 2s electrons reside mostly in the interstitial regions between the Li_2 units (Figure 14a).[107] This situation creates a beautiful high-pressure counterpart of the class of materials known to chemists as electrides.[108] A symmetry-breaking transition has indeed been observed for lithium under pressure (roughly between 40 and 50 GPa;[87b] Figure 14b). Though the structure found is somewhat different than theory had predicted,[109] the unexpected deformation highlights the importance of theoretical work in high-pressure science.

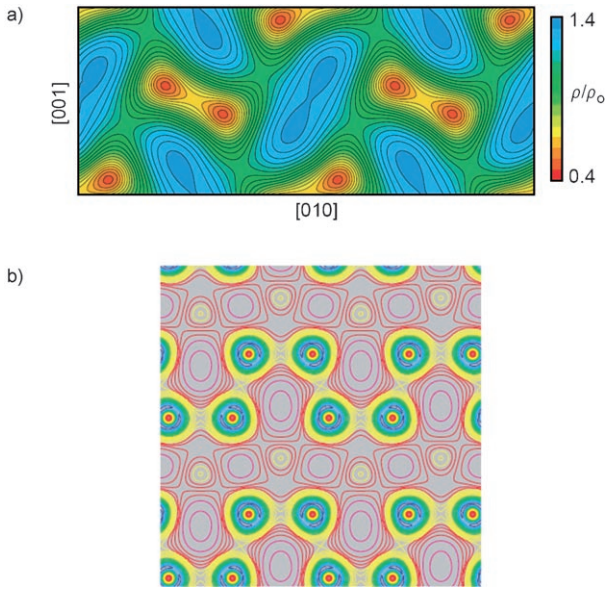

Figure 14. a) Calculated valence-electron density of the predicted pairing phase of lithium under pressure ($r_s = 2.0$ bohr; r_s is defined by $4\pi r_s^3/3 = 1/\rho$, where ρ is the average valence-electron density). The atoms are located at the regions of lowest valence-electron density (orange spots). b) Calculated valence-electron density in the actual lithium phase under high pressure (45 GPa; $\rho = 0.116$ e Å^{-3}). The color scheme for electron density goes from blue (low) to red (high). Reproduced by permission.[87b]

Good metals such as lithium *may*, in some pressure regime where the paired state prevails, become semiconducting or insulating.[110] Pairing is also predicted to be persistent in dense hydrogen phases, in which case it is predicted to be accompanied by charge transfer between hydrogen atoms,

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marking an onset of ionicity, albeit small, in elemental molecular hydrogen.[111]

Peierls instability can also arise as the structure of a compound changes with increasing pressure, either continuously or abruptly. The band structure (and hence the Fermi surface) change with changing structure. Neaton and Ashcroft found that the nesting vectors[87a] may gain in importance or new ones may emerge, resulting in *pressure-induced Peierls distortions*. Insulators and semiconductors may also be subject to second-order instabilities, but usually they are not distorted, because the stabilization from the Peierls distortion alone is insufficient. On a speculative note, the situation may change under pressure, where the band gap can be reduced with compression, raising the distortive energy stabilization.

More can be learned from the same simple metal, lithium. Bergara, Neaton, and Ashcroft[112] found in their calculations that the 2s and 2p bands of lithium scale very differently with density. In both all-electron local-density approximation (LDA) and valence-only nonlocal pseudopotential calculations, the 2p band broadened as expected, while the 2s band actually flattened—a phenomenon that was not seen in a valence-only LDA calculation with a local pseudopotential. This behavior was rationalized by an argument that the core state, 1s in this case, affects the 2s and 2p states differently. Apart from the Hartree screening, the core state also imposes orthogonality constraints on the valence states (the nonlocal projector of the pseudopotential). As the pseudopotential projects out only s character, orbitals with p symmetry (the 2p states) experience the full nuclear and Hartree potentials, while the 2s orbitals are affected differently.

This circumstance may, we hypothesize, account in part for the difference in behavior between the elements of Period 2 and the elements of higher periods under pressure: both the valence s and p states are affected by the core states for the elements of Period 3 and higher. Moreover, a similar scenario may apply when atomic orbitals with a higher angular-momentum quantum number are made available (for example, in the 3d metals).

The conclusion here is again not a rough rule as much as a warning: **H) Under extremely high pressure, electrons may move off atoms, and new "non-nucleocentric" bonding schemes need to be devised.**

14. Close Packing Is Not Close Enough

Space is the paramount issue when there is a lot of squeezing. What structure do the elements adopt under high pressure? The instinctive reaction is that they all are likely to favor close-packed structures (face-centered cubic (fcc), hcp, or variants thereof). Work of the last decade has proven this supposition incorrect.

The structure of Rb-IV (Figure 15) is a case in point.[113] As shown, the rubidium atoms segregate into two structural components: one consists of tubes constructed from edge-fused boat-shaped hexagons (green); the other consists of chains of atoms (blue), which thread through the tubes. These two sublattices are incommensurate. Similar phases have so far been observed for potassium, strontium, barium, arsenic, antimony, bismuth, and tellurium. In some of these host–guest structures, one can actually observe a differential "melting" of the linear thread. As another example of the sequence of transformations that can take place, consider barium: under pressure, barium goes from a bcc phase via an hcp phase to an incommensurate lower-symmetry form.[114]

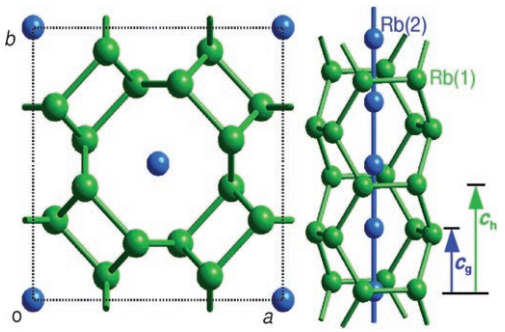

Figure 15. Two views of the crystal structure of Rb-IV at 17.2 GPa. The two sublattices (green and blue) have incommensurate periodicities in the *c* direction (c_h and c_g for the host and guest sublattices, respectively).

Here's one way to think about the fact that close packing is not close enough: the packing of equal-sized spheres maximizes at approximately 74% ($\pi/\sqrt{18}$) of the available space in the ideal hcp and fcc (that is, hexagonal and cubic close-packed) structures we know so well and their polytypes. If spheres are deformed, they can pack more efficiently, as shown by work on ellipsoids and M&M's,[115] and by the trivial case of extreme deformation to cubes. Or, if cubes are not to your taste, then to triangular or hexagonal prisms, to truncated octahedra, or to rhombic, elongated, or squashed dodecahedra. Nature does not like cusps in the electron density (except at the locus of nuclei, where they must be), but one can approach these pointy geometries quite gently …

Furthermore, the problem of the optimal packing of spheres of unequal size is unsolved, but it is obvious that for some radius ratios unequal-sized spheres may pack more efficiently than equal-sized spheres. There's a lot of room, so to speak, between 74 and 100%, if sphere sizes are allowed to vary continuously.

So … at some pressure, there may be a driving force for a lattice of element E to "electronically disproportionate" to sublattices, that is $(E^{\delta+})_m(E^{\delta-})_n$. Such sublattices could be of any dimensionality; there could be more than two sublattices. And, in principle, such sublattices could pack more efficiently.

Electron transfer between the sublattices may not be needed to differentiate them. One could imagine a disproportionation to sublattices A, B, and C, where each is roughly neutral, but is characterized by a different kind of bonding—covalent, ionic, or metallic. One is reminded here of the "Swiss-cheese" metallic alkali-metal suboxides, for example, Rb_9O_2 or $Cs_{11}O_3$.[116] One of us has suggested the existence of interpenetrating covalent and ionic sublattices in intermetallics such as $NaCd_2$.[117]

A disproportionation has been postulated for hydrogen under pressure.[118] In the IR spectrum of hydrogen at high pressures, there is indeed a striking enhancement of the intensity of the H_2 stretching mode (corresponding to a

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modest polarization),[119,120] in excess of what might have been expected simply on the basis of intermolecular perturbations.[121] Computations imply that a spontaneous polarization of H_2 occurs at around ninefold compression.[122]

We come to a rough rule: **I) Close packing is the way, for a while. But keep an open mind—still denser packing may be achieved through electronic disproportionation and through nonclassical deformation of spherical electron densities.**

15. Virtual Atomic Orbitals on Stage

The phenomena described so far can be thought about in a pretty classical chemical way (expanded to include the Peierls distortion). Implicit in this approach, virtually unvoiced, is a separation of the system (be it molecular or extended) into certain "neutral" or "ionic" building blocks, each of them adopting well-known electronic configurations. A typical ordering of the atomic levels is assumed (for example, the *n*p set lying above the *n*s orbitals), with perturbations (such as the *n*d orbitals of a transition-metal cation coming below the $(n+1)$s orbitals, in contrast to the ordering of the orbitals of neutral transition-metals atoms) being well-understood.[123]

However, various high-pressure phenomena exist which are associated with a significant degree of electron transfer from one electronic subshell to another. Such a process may require great energy at ambient pressure, so it doesn't enter the ambient-pressure-founded chemical imagination. Yet there are cases when explicit inclusion of such normally higher-lying virtual orbitals is *indispensable* for the qualitative understanding of a system's properties at high pressure.

Take EuO. Upon modest compression (at greater than 30 GPa), an unexpected 4f→5d promotion takes place, which leads to the pressure-induced metallization of this compound.[124] The europium cation becomes formally trivalent ($Eu^{III}O^{2-}e^-$), as the electrons in the 5d band are itinerant. When one attempts to model this transition, one is forced to consider 5d functions, along with the standard set of unoccupied 6s and 6p orbitals. Yet even this unusual transformation can be understood, by recalling the "valence fluctuations" which are well-known from the chemistry of certain lanthanides, or by remembering the rich photochemistry of lanthanide ions.

There are, however, high-pressure transformations (in particular, for "electronically soft" species, such as the heavier alkali metals and other relativistic atoms) that are outside of usual chemical experience, for they are associated with pronounced changes in electronic occupation. For example, the electronic configuration of compressed xenon is close to $5p^{5.63}5d^{0.37}$ at 140 GPa.[125] The substantial occupation of the 5d orbitals leads to a significant flattening of the melting curve of xenon. It is likely that the 5d orbitals make the electronic density on a xenon atom more labile and prone to more diverse secondary interactions; as a consequence, xenon easily adopts the high coordination number of $6+2$ in the resulting hcp structure. It turns out that d orbitals *must* be considered to explain anomalies of the melting curves of other seemingly s/p metals, such as aluminum,[126] and to explain the superconductivity of yttrium, lanthanum, and lutetium.[127]

Or take cesium and rubidium: these prototypical s/p-band nearly free-electron metals transform easily (at 4.2–15 GPa for cesium and at 53 GPa for rubidium) into d-electron conductors, with the occupation of the valence d orbitals even exceeding 0.5![128] Some of their phases show unusually complex bonding patterns and exhibit a counterintuitive decrease of the coordination number. Potassium becomes a d-electron metal at much higher pressure, while sodium shows a range of phases with unexpectedly low melting points at pressure less than 1 Mbar.[129]

Thus: **J) Pressure may cause the occupation of orbitals that a chemist would not normally think are involved.**

The structure and content of Mendeleev's Periodic Table of the Elements has been of obvious importance in guiding our chemical intuition for 140 years. This chemical masterpiece was largely deduced from the regularities of the elements in combination,[130] these trends being recorded under what we might reasonably call normal conditions, especially with respect to pressure. It is of some interest to ask how these regularities, and with them the deduced Periodic Table, might have changed had the "normal condition" of pressure been perhaps on the order of 1 000 000 atm or more.[131] Though this question may justifiably be seen as "terrestrially implausible", it has considerable relevance to the exercise being pursued here, which in a sense turns the question around. We examine compounds at high pressure from which one might, in a separate analysis, deduce at least a fragment of a high-pressure Periodic Table.

16. Rife with Speculation

All the cases discussed so far have been, in fact, connected to the appearance of *new* polymorphs of *known* chemical substances, with modest alterations of the electronic structure (so that oxidation states were preserved). But what about entirely new materials, especially if we can bring them back to 1 atm? And what about the stabilization of rare oxidation states of chemical elements? The *synthesis of new compounds* is at the very heart of chemistry.

It turns out that ultrahigh-pressure synthesis (so far lacking mass-scale applications, owing to the large costs of maintaining pressure and the necessity to operate on very small sample volumes) has given us some beautiful examples of stoichiometries which are completely unknown—and seemingly weird—at ambient pressure. A list of such compounds includes Fe_2S and Fe_3S,[132] Fe_3S_2,[133] and MN_2 (M = Pt,[134] Ir,[135] Os[136]). Some of these, such as Fe_2S and Fe_3S, are recoverable on quenching to ambient pressure and temperature. Others, such as Fe_3S_2, are not. Another example is provided by clathrates. Clathrate hydrates of methane and other alkanes are, of course, a natural and important part of the deep-sea and mantle environments.[137] Still other clathrates, not (yet) known in nature, have been characterized in the laboratory.[138]

Considering the metastability issue, a chemist might be intrigued to know why Fe^{I}_2S, with its unusual monovalent cation, doesn't disproportionate to the more "typical" species $Fe^{II}S$ and Fe^0. Are there large activation barriers to some of

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these processes, and could they be understood within the framework of the orbital-symmetry control of chemical reactions? And could Na_2Cl be synthesized by means of pressure alone?[139]

Our imagination can roam further. Might one achieve one day a metastable insulating $Au^{I}Au^{-}$ polymorph of gold,[140] which is a prototypical electronic conductor? Could $Si^{IV}(O^{2-})_2$, $Ge^{IV}(O^{2-})_2$ (Figure 16a), and other homologous

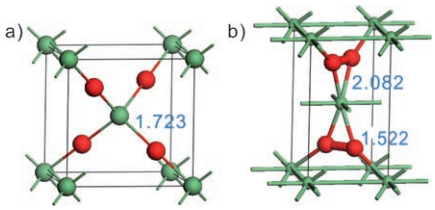

Figure 16. Comparison of the optimized (for 0 GPa) unit cells (Ge green, O red) of a) $Ge^{IV}(O^{2-})_2$ in a cubic anti-Cu_2O structure ($Pn\bar{3}m$, no. 224) and b) $Ge^{II}(O_2^{2-})$ in a related tetragonal structure ($P\bar{4}2m$, no. 111).[144] The Ge–O and O–O bond lengths [Å] are indicated. The oxide form is calculated to be favored by about 10 eV per cell ($Z=2$) over the peroxide; the oxide also has a significantly smaller cell volume. Therefore, the structure in (b) is a hypothetical "negative-pressure" form. Peroxide polymorphs might be stabilized relative to the oxides for strong oxidizers (such as PbO_2 or $KMnO_4$), possibly under high pressure.

compounds (in particular, strong oxidizers, such as PbO_2, $KMnO_4$, $BaCrO_4$, or $BaFeO_4$) form a pyrite-like $M^{II}(O_2^{2-})$ peroxide compound (Figure 16b) under appropriate conditions?[141] One might try Be_2SiO_4 (phenakite) or $AlBO_3$, which have some of the shortest nonbonded O···O contacts in their ambient-pressure structures. What pressure is necessary to increase the ligand field sufficiently to turn prototypical high-spin compounds of Fe^{III} (a d^5 "pentaradical") into low-spin compounds?[142] Or maybe even to form Fe–Fe multiple bonds? And can one drastically alter the ordinary regimes of spin–orbit coupling under pressure?[143]

Could $[N^{III}O]^{+}[N^{V}O_3]^{-}$ [145,146] (or $[CO]^{2+}[CO_3]^{2-}$ [147]) melts be rapidly quenched to yield novel high-energy ionic polymorphs of $N^{IV}O_2$ (or CO_2)? To what extent might $W^{VI}N_2$[80] be stabilized (and the formation pressure decreased) when in a ternary phase, such as $LaWN_3$ or La_2WN_4?[148] Could one resynthesize hexagonal CuH, which decomposes to its component elements at a pressure of about 8 GPa,[149] at even higher pressures? And what basic chemistry underlies the polymerization of the N^{3-} ions in NaN_3 at high pressure?[150] Could one achieve a broad range of novel species featuring bonds between noble-gas and transition-metal atoms at high pressure?[151] What pressures are required to transform the lanthanides from inner transition metals into "true" outer transition metals, that is, for the involvement of the (otherwise contracted) f shell in bonding to become significant,[152] by analogy to the softer actinides?[153,154] Could "aurophilic interactions" (or their copper and silver analogues) evolve into genuine Au^{I}–Au^{I} bonding at high pressure? How large a pressure is needed for comproportionation of Au^0 and $Au^{III}F_3$ into the scarce species $Au^{I}F$?[155] And could ice—possibly slightly doped with NH_3 or HF, by analogy with known nonstoichiometric solid ion conductors—become a superionic conductor at extremely high pressure and temperature?[156]

These speculations are wild. But as we have pointed out, strange things happen in the realm of high pressure. Strange, but consistent with the chemical imagination. There is more to come.

Appendix A. An Introduction to Electron-Rich and Electron-Poor Three-Center Bonding

If we have a system of three basis orbitals—in a linear, bent, or triangular arrangement—we get three MOs, as shown for three s orbitals in Figure 17 (top). Orbitals of other symmetry may also participate in such bonding, as shown for a p orbital of the central atom in Figure 17 (bottom).

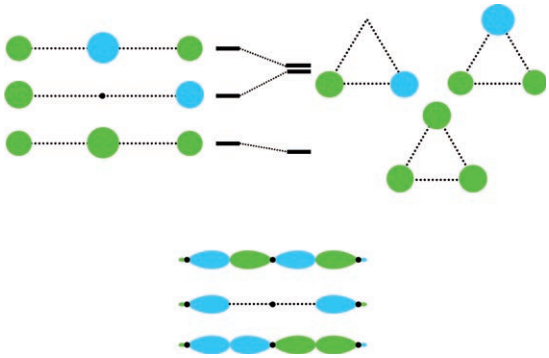

Figure 17. Several three-center bonding schemes. Top: three s orbitals in a linear (left) and a triangular (right) arrangement. Bottom: two hybrid orbitals on terminal atoms and a p orbital on the central atom in a linear arrangement. These are limiting schemes; a more realistic description involves the admixture of p orbitals (top) or of s orbitals (bottom) at the central atom.

In come electrons. For either two electrons (electron-deficient) or four electrons (electron-rich), the three centers are bonded together. So one accounts for the bonding in the central region of diborane by two electron-deficient three-center bonds, and explains the axial bonding in PF_5 by one electron-rich three-center bond. Electron-deficient bonding is not restricted to the boron group; it also holds together the quite stable protonated H_3^{+} and CH_5^{+} molecules. And is involved in agostic interactions. Electron-rich bonding cuts a wide swath across the right side of the Periodic Table; it is found in the molecular structures of SF_4, ClF_3, and XeF_2, and also in many extended structures, for instance, in the linear Sb^{-} infinite chains of LiSb, and the Sb^{2-} square nets in $BaZnSb_2$.[42]

Note that with the electron count comes a geometrical preference. As the Walsh diagram for "open" and "closed" three-center bonding (Figure 17, top) shows, a two-electron system (for example, H_3^{+}) would prefer a triangular geometry. But the slope of the second level dictates a linear geometry for a four-electron system (for example, H_3^{-}). Less obvious,

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but still possible to show, is that these preferences are reversed for a central p orbital (Figure 17, bottom).

The two bonding types we discuss here (electron-rich and electron-poor) seem quite distinct. Their difference is maximal for three centers (for example, I_3^+ versus I_3^-). For more centers (for example, I_{2n+1}^+ versus I_{2n+1}^-, for large n), the bonding schemes approach each other. In the limit, bonding is maximized for one electron per center (there may also be unshared electron pairs). There's a relation here to the conditions for a Peierls distortion.

Appendix B. An Introduction to the Peierls Distortion

Here we introduce the basic idea of a Peierls distortion. Consider an infinite linear periodic chain of static hydrogen atoms separated by a distance a, each carrying only its valence 1s orbital. The energy levels of such a hydrogen polymer form a band (Figure 18, left). The corresponding MOs range from

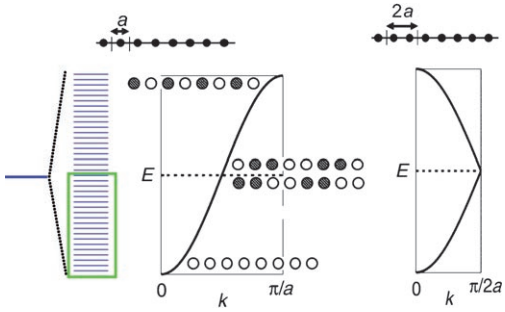

Figure 18. Energy band of a chain of hydrogen atoms with regular spacing. The atomic level spreads out into a band of closely spaced levels (left; the green box indicates the filled levels). The band is plotted as $E(k)$ versus k for a chain with one atom per unit cell (middle; some MOs at the bottom, middle, and top of the band are shown). The same band is folded back for a chain with two atoms per unit cell (right). The dashed lines indicate the Fermi level.

one with no nodes (at the bottom of the band), through nonbonding ones (a degenerate pair in the middle of the band), to a combination with the most nodes possible (at the top of the band). These levels are often labeled by the symmetry of the wavefunctions (the irreducible representations of the translational symmetry group), which in turn are actually a variable, the wavenumber k (wavevector in higher dimensions) in reciprocal space.[157]

The band can, thus, be drawn in another way, as a plot of $E(k)$ versus k (Figure 18, middle), which is called the electronic band structure. The range of unique values of k is called the first Brillouin zone. Since $E(k) = E(-k)$, it is customary to plot only the unique values of the energy, that is, those for positive k values. Every level inside the zone is degenerate.[158]

When there is only one electron per atom, as is the case for hydrogen in the ground state, exactly half of these levels (up to the Fermi level) are filled by a pair of electrons. Every chemist feels intuitively that such a chain of hydrogen atoms (at ambient pressure) would pair into H_2 molecules. To appreciate the electronic origin of this instability of the chain, let's look at what happens to the MOs at the Fermi level upon distortion.

If pairing is to occur, the unit cell will be doubled. So to prepare for the potential distortion, we first redraw the band in a larger unit cell containing two hydrogen atoms, ergo in a smaller Brillouin zone. The MOs are the same as for the case of one hydrogen atom per unit cell, for (so far) no physical change has taken place (Figure 18, right). But the band is "folded back". Now we move the atoms off their sites to try out the pairing distortion. The effect is biggest for the degenerate orbital set (Ψ_1 and Ψ_2) right at the Fermi level. As shown in Figure 19, the pairing motion enhances the in-phase,

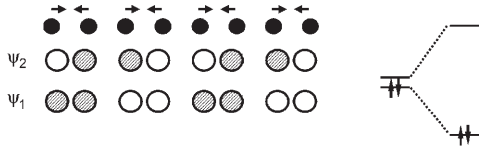

Figure 19. A pairing distortion of the chain of hydrogen atoms (left) causes the splitting of orbitals (for example, Ψ_1 and Ψ_2) at the Fermi level (right).

bonding overlap and lowers the out-of-phase overlap in Ψ_1. This outcome will lower the energy of Ψ_1. On the other hand, Ψ_2 is destabilized by the same pairing distortion—antibonding is turned on in the pair. While the strongest splitting occurs where there is strict degeneracy, that is, at the Fermi level, additional stabilization can be obtained from the interaction of filled bands with unfilled ones throughout **k** space, through second-order effects.

Fundamentally, levels which were degenerate (or nearly degenerate) and were occupied by two electrons split in energy. Were this process to happen in a molecule (for example, to the π system of cyclobutadiene or to an octahedrally coordinated d^9 Cu^{II} ion), we would call it a Jahn–Teller distortion, a coupling of the energy levels with a normal mode of vibration. In the extended system, the phenomenon is called a Peierls distortion, and is spoken about in terms of the coupling of electronic motions and lattice vibrations (phonons).

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[1] a) R. J. Hemley, N. W. Ashcroft, *Nature* **1996**, *380*, 671; b) R. J. Hemley, N. W. Ashcroft, *Phys. Today* **1998**, *51*, 26; c) J. S. Schilling, *Hyperfine Interact.* **2000**, *128*, 3; d) P. F. McMillan, *Nat. Mater.* **2002**, *1*, 19.

[2] R. J. Hemley, *Annu. Rev. Phys. Chem.* **2000**, *51*, 763. Pressures on the order of 10 GPa are now considered as "moderate vacuum" by the high-pressure community.

[3] R. Boehler, M. Ross, P. Soderlind, D. B. Boercker, *Phys. Rev. Lett.* **2001**, *86*, 5731. Even H_2, one of the most volatile and hard-to-solidify liquids, is a solid that melts above 600 °C at such pressures. The melting points of some substances (such as diamond and H_2) are predicted to reach a maximum with increasing pressure, possibly indicating their tendency to undergo amorphization at even larger pressures: S. A. Bonev, E. Schwegler, T. Ogitsu, G. Galli, *Nature* **2004**, *431*, 669; A. A. Correa, S. A. Bonev, G. Galli, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 1204.

[4] For very soft matter, such as helium or H_2, the volume reduction may exceed a factor of 5 at an even smaller pressure of 50 GPa: P. Loubeyre, R. Letoullec, J. P. Pinceaux, H.-k. Mao, J. Hu, R. J. Hemley, *Phys. Rev. Lett.* **1993**, *71*, 2272. For moderately soft CsH, the volume reduction at 200 GPa is by a factor of 2.5: K. Ghandehari, H. Luo, A. L. Ruoff, S. S. Trail, F. J. DiSalvo, *Solid State Commun.* **1995**, *95*, 385. For substances with much smaller compressibility, such as ZnO or aluminum, the volume reduction is less than twofold: Y. Mori, N. Niiya, K. Ukegawa, T. Mizuno, K. Takarabe, A. L. Ruoff, *Phys. Status Solidi B* **2004**, *241*, 3198; R. G. Greene, H. Luo, A. L. Ruoff, *Phys. Rev. Lett.* **1994**, *73*, 2075. An analytic relationship that unifies the equation-of-state curves for many different elements and compounds has been proposed: A. M. Molodets, *High Pressure Res.* **2005**, *25*, 267.

[5] The field has grown incredibly. As an example of the depth of the research in the area, we cite here just one review, on just one substance, albeit an important one—hydrogen under pressure: H.-k. Mao, R. J. Hemley, *Rev. Mod. Phys.* **1994**, *66*, 67.

[6] The reader will find many reviews in the literature, after P. W. Bridgman's pioneering work. We mention here just two: A. Jayaraman, *Rev. Mod. Phys.* **1983**, *55*, 65; H. G. Drickamer, *Annu. Rev. Mater. Sci.* **1990**, *20*, 1. See also the special issue on chemistry at high pressure: *Chem. Soc. Rev.* **2006**, 845–1016.

[7] Our discussion will not deal specifically with the consequences of pressure on the spin variable, that is, on magnetism; the arguments presented here can be carried over, albeit with complications, to the fascinating area of magnetic structure in the realm of high pressure.

[8] J. Feng, W. Grochala, T. Jaroń, R. Hoffmann, A. Bergara, N. W. Ashcroft, *Phys. Rev. Lett.* **2006**, *96*, 017006.

[9] This polymerization is particularly easy for CO, C_2H_2, $(CN)_2$, CS_2, and the like. Even aromatic benzene transforms to a disordered cross-linked polymer at 30 GPa: Ph. Pruzan, J. C. Chervin, M. M. Thiéry, J. P. Itié, J. M. Besson, J. P. Forgerit, M. Revault, *J. Chem. Phys.* **1990**, *92*, 6910. See also: V. Schettino, R. Bini, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1951, and references therein.

[10] The existence of a quartz-like structure with four-coordinate carbon atoms is unambiguous, but it has not proven easy to reach a consensus on its structure—is it of the tridymite or cristoballite type? See: V. Iota, C. S. Yoo, H. Cynn, *Science* **1999**, *283*, 1510; C. S. Yoo, H. Cynn, F. Gygi, G. Galli, V. Iota, M. Nicol, S. Carlson, D. Häusermann, C. Mailhiot, *Phys. Rev. Lett.* **1999**, *83*, 5527; J. Dong, J. K. Tomfohr, O. F. Sankey, K. Leineweber, M. Somayazulu, P. F. McMillan, *Phys. Rev. B* **2000**, *62*, 14685; B. Holm, R. Ahuya, A. Belonoshko, B. Johansson, *Phys. Rev. Lett.* **2000**, *85*, 1258. See also: O. Tschauner, H.-k. Mao, R. J. Hemley, *Phys. Rev. Lett.* **2001**, *87*, 75701. For CO_2-IV, there is a controversy on whether the phase contains linear or bent discrete molecules: J.-H. Park, C. S. Yoo, V. Iota, H. Cynn, M. F. Nicol, T. Le Bihan, *Phys. Rev. B* **2003**, *68*, 014107; F. A. Gorelli, V. M. Giordano, P. R. Salvi, R. Bini, *Phys. Rev. Lett.* **2004**, *93*, 205503; S. A. Bonev, F. Gygi, T. Ogitsu, G. Galli, *Phys. Rev. Lett.* **2003**, *91*, 065501.

[11] M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, R. Boehler, *Nat. Mater.* **2004**, *3*, 558; M. I. Eremets, R. J. Hemley, H.-k. Mao, E. Gregoryanz, *Nature* **2001**, *411*, 170, and references therein. A small amount of material was recoverable upon return to ambient pressure at a temperature below 50 K.

[12] A. F. Goncharov, V. V. Struzhkin, H-k. Mao, R. J. Hemley, *Phys. Rev. Lett.* **1999**, *83*, 1998; M. Bernasconi, P. L. Silvestrelli, M. Parinello, *Phys. Rev. Lett.* **1998**, *81*, 1235.

[13] Kurt Vonnegut, of "ice IX" fame (K. Vonnegut, Jr., *Cat's Cradle*, Dell, New York, **1970**), was a chemistry and biology major at Cornell.

[14] S. J. Rettig, J. Trotter, *Acta Crystallogr. C* **1987**, *43*, 2260.

[15] O. Degtyareva, E. Gregoryanz, M. Somayazulu, P. Dera, H.-k. Mao, R. J. Hemley, *Nat. Mater.* **2005**, *4*, 152, and references therein.

[16] G. A. Landrum, N. Goldberg, R. Hoffmann, *J. Chem. Soc. Dalton Trans.* **1997**, 3605.

[17] V. V. Struzhkin, R. J. Hemley, H.-k. Mao, Y. A. Timofeev, *Nature* **1997**, *390*, 382.

[18] S. P. Rudin, A. Y. Liu, *Phys. Rev. Lett.* **1999**, *83*, 3049.

[19] O. Zakharov, M. L. Cohen, *Phys. Rev. B* **1995**, *52*, 12572.

[20] This relationship was observed and utilized long ago in studies of silicate minerals of geophysical importance. Researchers would then rather explore the analogous germanates, for which similar phase transitions were observed at much more modest pressures. However, with the progress in high-pressure anvils, phase transitions in silicates can now be studied.

[21] An extended version of these rules is available in: C. T. Prewitt, R. T. Downs, *Rev. Mineral.* **1998**, *37*, 283 ("High-Pressure Crystal Chemistry").

[22] L. Pauling, *The Nature of the Chemical Bond*, *3rd ed.*, Cornell University Press, Ithaca, **1960**, chap. 13.

[23] Interesting exceptions from these rules are known. For example, after a sequence of phase transitions, gallium transforms at 120 GPa into the fcc structure, which is then stable up to at least 150 GPa. Smaller aluminum adopts the fcc structure at 1 atm, while larger thallium adopts the hcp structure: T. Kenichi, K. Kazuaki, A. Masao, *Phys. Rev. B* **1998**, *58*, 2482.

[24] J. B. Goodenough, J. A. Kafalas, J. M. Longo in *Preparative Methods in Solid State Chemistry* (Ed.: P. Hagenmuller), Academic Press, New York, **1972**, pp. 1–69 ("High-Pressure Synthesis").

[25] S. Shaik, D. Danovich, B. Silvi, D. L. Lauvergnat, P. C. Hiberty, *Chem. Eur. J.* **2005**, *11*, 6358.

[26] The contribution of electronic correlation is difficult to quantify, even for small systems. It would be very interesting to know how electronic correlation changes upon systematic application of pressure to, say, an LiH crystal.

[27] This picture applies only for electrons with small kinetic energies. At sufficiently great compression, the kinetic energy component may take over and (at least some) electrons may become itinerant. The balance of the potential and kinetic energy of electrons in the chemical bond is important even at low pressure: a) K. Ruedenberg, *Rev. Mod. Phys.* **1962**, *34*, 326; b) N. C. Baird, *J. Chem. Educ.* **1986**, *63*, 660; c) W. Kutzelnigg in *Theoretical Models of Chemical Bonding*, *Vol. 2* (Ed.: Z. B. Maksić), Springer, Berlin, **1990**, pp. 1–44.

[28] W. Kutzelnigg, *Angew. Chem.* **1973**, *85*, 551; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 546.

[29] K. P. Huber, G. Herzberg, *Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, **1979**. The bond shortening

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in these excited states is well-understood; it derives from a good single-configuration description of the excited state as a $\sigma_u \rightarrow \sigma_g$ excitation, where σ_u and σ_b are both essentially lone-pair combinations, the first slightly antibonding, the second slightly bonding.

[30] For an amusing competition to design a very short, indeed squeezed C–C bond, see: D. Huntley, G. Markopoulos, P. M. Donovan, L. T. Scott, R. Hoffmann, *Angew. Chem.* **2005**, *117*, 7721; *Angew. Chem. Int. Ed.* **2005**, *44*, 7549.

[31] The calculation was performed using the program Gaussian 03, with a B3LYP correlation–exchange functional and the standard 6-311++G** basis set.

[32] There are certain types of orbital overlaps (for example, p–p σ and s–p σ) which do not increase uniformly on compression, but which go through a maximum.

[33] See: G. V. Gibbs, F. C. Hill, M. B. Boisen, R. T. Downs, *Phys. Chem. Miner.* **1998**, *25*, 585.

[34] M. Hanfland, R. J. Hemley, H.-k. Mao, *Phys. Rev. Lett.* **1993**, *70*, 3760, and references therein.

[35] See the reviews cited in ref. [6].

[36] Interestingly, and in contrast to the fluoride–hydride analogy, NF_5 *is* a local minimum on its potential-energy surface.

[37] a) R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533; b) R. G. Pearson, *Acc. Chem. Res.* **1993**, *26*, 250.

[38] The initial eigenfunctions (at ambient pressure, say) are, of course, orthonormal. These functions are no longer orthogonal when carried over to a compressed geometry. When they then serve as zero-order functions for a perturbation treatment, they may mix with each other.

[39] A clear indication of this phenomenon (explained in just the way we forward here) is found in the specifics of the high-pressure disruption of benzene molecules: L. Ciabini, M. Santoro, R. Bini, V. Schettino, *Phys. Rev. Lett.* **2002**, *88*, 085505; V. Schettino, R. Bini, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1951.

[40] Cases are known (including diamond and MgO) in which the band gap increases at elevated pressure.

[41] For example, the formally unoccupied 5d orbitals come into play when xenon is under high pressure (see Section 15). The addition of d orbitals to the s/p set allows xenon to achieve different bonding patterns.

[42] G. A. Papoian, R. Hoffmann, *Angew. Chem.* **2000**, *112*, 2500; *Angew. Chem. Int. Ed.* **2000**, *39*, 2409.

[43] a) R. J. Gillespie, R. S. Nyholm, *Q. Rev. Chem. Soc.* **1957**, *11*, 339; b) R. F. W. Bader, R. J. Gillespie, P. J. Macdougall, *J. Am. Chem. Soc.* **1988**, *110*, 7329.

[44] The contributors to establishing the beautiful construct of three-center bonding include H. C. Longuet-Higgins, G. C. Pimentel, R. E. Rundle, W. N. Lipscomb, K. S. Pitzer, and others.

[45] Ionic compounds have less trouble forming hypervalent bonds, even at ambient pressure. The symmetric "ionic" species HF_2^- and the family of asymmetric more covalently bound species $HO{-}H{\cdots}OH^-$, $H_2N{-}H{\cdots}NH_2^-$, and $H_3C{-}H{\cdots}CH_3^-$ testify to that. In this way, four-electron three-center bonding makes a nice link with the three-electron three-center bonding in molecular radicals: W. Grochala, R. Hoffmann, *Pol. J. Chem.* **2001**, *75*, 1603.

[46] W. Müller, *Z. Naturforsch. B* **1977**, *32*, 3257.

[47] See ref. [42].

[48] C. J. Pickard, R. J. Needs, *Phys. Rev. Lett.* **2006**, *97*, 045504.

[49] M. Martinez-Canales, A. Bergara, J. Feng, W. Grochala, *J. Phys. Chem. Solids* **2006**, *67*, 2095.

[50] To maintain as much generality as possible, no restrictions were placed upon either the oxidation state or the coordination numbers of the atoms involved in the bonds.

[51] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272; A. E. Reed, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 1434, and references therein.

[52] See, for instance, the orbitals of BrH_n ($n = 3$–6): L. Subramanian, R. Hoffmann, *Inorg. Chem.* **1992**, *31*, 1021.

[53] R. B. Woodward, R. Hoffmann, *Angew. Chem.* **1969**, *81*, 797; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781; reprinted in book form by Verlag Chemie and Academic Press.

[54] See, for example: R. Bini, *Acc. Chem. Res.* **2004**, *37*, 95.

[55] In ref. [11], it is reported that small quantities of amorphous polymeric material have been recovered at near-ambient pressure at a temperature below 50 K.

[56] Substitution may be a general strategy. It has been implemented in high-pressure materials synthesis, for instance, of $LiV_xNb_{1-x}O_3$: A. Grzechnik, P. F. McMillan, *J. Phys. Chem. Solids* **1997**, *58*, 1071.

[57] See, for instance: V. Brazhkin, A. G. Lyapin, *Nat. Mater.* **2004**, *3*, 497.

[58] V. Schettino, R. Bini, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1951.

[59] M. Somayazulu, A. Madduri, A. F. Goncharov, O. Tscauner, P. F. McMillan, H-k. Mao, R. J. Hemley, *Phys. Rev. Lett.* **2001**, *87*, 135504; C. S. Yoo, V. Iota, H. Cynn, M. Nicol, T. Le Bihan, M. Mezouar, *J. Phys. Chem. B* **2003**, *107*, 5922.

[60] S. Benard, G. L. Chiarotti, S. Scandolo, E. Tosatti, *Phys. Rev. Lett.* **1998**, *81*, 2092; M. J. Lipp, W. J. Evans, B. J. Baer, C. S. Yoo, *Nat. Mater.* **2005**, *4*, 211; W. J. Evans, M. J. Lipp, C. S. Yoo, H. Cynn, J. L. Herberg, R. S. Maxwell, M. F. Nicol, *Chem. Mater.* **2006**, *18*, 2520.

[61] D. L. Heinz, R. Jeanloz, *Phys. Rev. B* **1984**, *30*, 6045; X. Li, R, Jeanloz, *Phys. Rev. B* **1987**, 36, 474.

[62] The nominal value of the pressure is, of course, negative for the B2–B1 transformation of the cesium halides and of RbF.

[63] a) R. Boehler, M. Ross, D. B. Boercker, *Phys. Rev. Lett.* **1997**, *78*, 4589; b) A. B. Belonoshko, R. Ahuja, B. Johansson, *Phys. Rev. Lett.* **2000**, *84*, 3638.

[64] Trends in the relation between the transition pressure and the crystal ionicity, and between the transition pressure and the ratio of the ionic radii of the anion and cation have been anticipated: C. Narayana, V. J. Nesamony, A. L. Ruoff, *Phys. Rev. B* **1997**, *56*, 14338.

[65] M. O'Keeffe, B. G. Hyde, *Structure and Bonding in Crystals* (Eds.: M. O'Keeffe, A. Navrotsky), Wiley, New York, **1981**, chap. 10; M. O'Keeffe, B. G. Hyde, *Struct. Bonding* **1985**, *61*, 77.

[66] a) L. Pauling, *Proc. R. Soc. London Ser. A* **1927**, *114*, 181; b) S. S. Jaswal, T. P. Sharma, *J. Phys. Chem. Solids* **1973**, *34*, 509.

[67] J. S. Nicoll, G. V. Gibbs, M. B. Boisen, R. T. Downs, K. L. Bartelmehs, *Phys. Chem. Miner.* **1994**, *20*, 617.

[68] We are referring to a "differential compressibility", the diminution in the size of an anion relative to that of a cation.

[69] R. Jeanloz, T. J. Ahrens, H.-k. Mao, P. M. Bell, *Science* **1979**, *206*, 829.

[70] H. Z. Liu, H.-k. Mao, M. Somayazulu, Y. Ding, Y. Meng, D. Häusermann, *Phys. Rev. B* **2004**, *70*, 094114.

[71] H. Luo, K. Ghandehari, R. G. Greene, A. L. Ruoff, S. S. Trail, F. J. DiSalvo, *Phys. Rev. B* **1995**, *52*, 7058.

[72] R. G. Greene, H. Luo, A. L. Ruoff, S. S. Trail, F. J. DiSalvo, *Phys. Rev. Lett.* **1994**, *73*, 2476.

[73] K. Ghandehari, H. Luo, A. L. Ruoff, S. S. Trail, F. J. DiSalvo, *Phys. Rev. Lett.* **1995**, *74*, 2264.

[74] A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fuess, P. Kroll, R. Boehler, *Nature* **1999**, *400*, 340.

[75] K. Leinenweber, M. O'Keeffe, M. Somayazulu, H. Hubert, P. F. McMillan, G. H. Wolf, *Chem. Eur. J.* **1999**, *5*, 3076.

[76] K. Landskron, H. Huppertz, J. Senker, W. Schnick, *Angew. Chem.* **2001**, *113*, 2713; *Angew. Chem. Int. Ed.* **2001**, *40*, 2643.

[77] A. K. Tyagi, J. Koehler, P. Balog, J. Weber, *J. Solid State Chem.* **2005**, *178*, 2620.

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[78] At ambient pressure, only one inorganic solid, $Be(BH_4)_2$, contains six-coordinate Be^{II}, while six-coordinate B^{III} has not been observed so far.
[79] Eight-coordinate Sc^{III} is found in the novel high-pressure phase $LiScF_4$: A. K. Tyagi, J. Koehler, P. Balog, J. Weber, *J. Solid State Chem.* **2005**, *178*, 2620.
[80] P. Kroll, T. Schröter, M. Peters, *Angew. Chem.* **2005**, *117*, 4321; *Angew. Chem. Int. Ed.* **2005**, *44*, 4249.
[81] C. N. Louis, K. Iyakutti, P. Malarvizhi, *J. Phys. Condens. Matter* **2004**, *16*, 1577.
[82] D. M. Teter, *MRS Bull.* **1998**, *23*, 22.
[83] To be precise, Wigner and Huntington say in a footnote (without further citation), "It was J. D. Bernal who first put forward the view that all substances go over under very high pressure into metallic or valence lattices." By "valence lattice", we think Bernal meant what we today call a covalent solid, such as diamond. E. Wigner, H. B. Huntington, *J. Chem. Phys.* **1935**, *3*, 764.
[84] The importance of static electronic dipole polarizability for the metallization of elements and compounds is most strongly emphasized by the Herzfeld–Goldhammer theory of metallization. This description dates back to 1927. See: a) D. A. Goldhammer, *Dispersion und Absorption des Lichtes in ruhenden isotropen Körpern*; *Theorie und ihre Folgerungen*, Teubner, Leipzig, **1913**; b) K. F. Herzfeld, *Phys. Rev.* **1927**, *29*, 701; c) S. S. Batsanov, *Refractometry and Chemical Structure*, Van Nostrand, New York, **1966**.
[85] Compare also: W. Grochala, R. Hoffmann, P. P. Edwards, *Chem. Eur. J.* **2003**, *9*, 575.
[86] W. Grochala, unpublished results (DFT GGA/PBE calculations; cut-off 310 eV; *k*-point sampling: $12\times12\times12$; ultrasoft pseudopotentials).
[87] Several remarkable exceptions from rule F are known, in which the ground-state metallic system turns insulating or semiconducting at a moderate pressure. Examples include the well-known transformation of graphite to diamond, the appearance of a semimetallic phase of Li_2 (somewhat analogous to molecular H_2), and a possible transformation of sodium into an insulator at pressures greater than 1000 GPa. See, for example: a) J. B. Neaton, N. W. Ashcroft, *Nature* **1999**, *400*, 141; b) M. Hanfland, K. Syassen, N. E. Christensen, D. L. Novikov, *Nature* **2000**, *408*, 174; c) F. Siringo, R. Pucci, G. G. N. Angilella, *High Pressure Res.* **1997**, *15*, 255.
[88] a) K. A. Goettel, J. H. Eggert, I. F. Silvera, W. C. Moss, *Phys. Rev. Lett.* **1989**, *62*, 665; b) R. Reichlin, K. E. Brister, A. K. McMahan, M. Ross, S. Martin, Y. K. Vohra, A. L. Ruoff, *Phys. Rev. Lett.* **1989**, *62*, 669. Krypton and argon have been predicted to metallize at, respectively, 310 and 510 GPa: c) I. Kwon, L. A. Collins, J. D. Kress, N. Troullier, *Phys. Rev. B* **1995**, *52*, 15165.
[89] a) M. I. Eremets, K. Shimizu, T. C. Kobayashi, K. Amaya, *Science* **1998**, *281*, 1333. The metallizations of CsI and of xenon have long been predicted by theory. Remarkably, CsH has withstood attempts at metallization up to 250 GPa, in agreement with the persistent fluoride–hydride analogy: b) K. Ghandehari, H. Luo, A. L. Ruoff, S. S. Trail, F. J. DiSalvo, *Solid State Commun.* **1995**, *95*, 385.
[90] T. A. Grzybowski, A. L. Ruoff, *Phys. Rev. Lett.* **1984**, *53*, 489.
[91] H.-k. Mao, Y. Wu, R. J. Hemley, L. C. Chen, J. F. Shu, *Science* **1989**, *246*, 649.
[92] See the various articles in: *Semiconductors and Semimetals*, *Vol. 54* (Eds.: T. Suski, W. Paul), Academic Press, New York, **1998** ("High Pressure in Semiconductor Physics I").
[93] See ref. [87a].
[94] a) S. Lei, D. A. Papaconstantopoulos, M. J. Mehl, *Phys. Rev. B* **2007**, *75*, 024512; b) J. Feng, unpublished results.
[95] H. A. Jahn, E. Teller, *Proc. R. Soc. London Ser. A* **1937**, *161*, 220; U. Opik, M. H. L. Pryce, *Proc. R. Soc. London Ser. A* **1957**, *238*, 425; L. Salem, *The Molecular Orbital Theory of Conjugated Systems*, Benjamin, New York, **1966**.
[96] For a good introduction to this way of analyzing crystal distortions, see: E. Canadell, M.-H. Whangbo, *Chem. Rev.* **1991**, *91*, 965.
[97] N. Kojima, N. Matsushita, *Coord. Chem. Rev.* **2000**, *198*, 251, and references therein.
[98] J. Grannec, L. Lozano, J. Portier, P. Hagenmuller, *Z. Anorg. Allg. Chem.* **1971**, *385*, 26.
[99] One intriguing observation is that, in some cases, there is no Peierls distortion in compounds which should show such distortion under ambient conditions (for example, the transparent metallic compound InO_{1+x} (approximately s^1), $Yb^{III}N$ (f^{13}), $Cu^{II}O$ (d^9), and $Ag^{II}F_2$ (d^9)).
[100] P. C. Hiberty, S. Shaik, *Theor. Chem. Acc.* **2005**, *114*, 169.
[101] We have not discussed here the real potential of another symmetry-breaking mechanism, a charge-density wave.
[102] T. Kenichi, S. Kyoko, F. Hiroshi, O. Mitsuko, *Nature* **2003**, *423*, 971.
[103] See also the discussion in ref. [42] of the deformations of square lattices in extended systems with six valence electrons.
[104] There are an infinite number of possible nesting vectors. It is usually the combination of nesting vectors that connect the largest number of points on the Fermi surface that gives rise to the observed Peierls distortion. A discussion of the real system should also include nesting vectors in three dimensions.
[105] Reversal of the Peierls distortion and the comproportionation of oxidation states are quite frequently encountered at elevated pressure, even for pretty exotic systems, such as Fe^{V}/Fe^{III} in $CaFeO_3$: M. Takano, S. Nasu, T. Abe, K. Yamamoto, S. Endo, Y. Takeda, J. B. Goodenough, *Phys. Rev. Lett.* **1991**, *67*, 3267. A brief review of such effects is given in: G. Demazeau, *J. Phys. Condens. Matter* **2002**, *14*, 11031.
[106] U. Schwarz, *Z. Kristallogr.* **2004**, *219*, 376.
[107] The 2s valence electrons cannot, of course, be entirely expelled outside the Li_2 unit; they must still be utilized for partial 2s–2s σ bonding.
[108] J. L. Dye, *Inorg. Chem.* **1997**, *36*, 3816.
[109] It is possible that experiment has not gone to high enough pressure to find the suggested structure.
[110] Superconductivity also appears in compressed lithium at the verge of the metal–insulator transition ($T_C\approx15$ K at about 30 GPa). See: S. Deemyad, J. S. Schilling, *Phys. Rev. Lett.* **2003**, *91*, 167001.
[111] B. Edwards, N. W. Ashcroft, *Nature* **1997**, *388*, 652.
[112] A. Bergara, J. B. Neaton, N. W. Ashcroft, *Phys. Rev. B* **2000**, *62*, 8494.
[113] M. I. McMahon, R. J. Nelmes, *Phys. Rev. Lett.* **2004**, *93*, 055501.
[114] R. J. Nelmes, D. R. Allan, M. I. McMahon, S. A. Belmonte, *Phys. Rev. Lett.* **1999**, *83*, 4081.
[115] A. Donev, F. H. Stillinger, P. M. Chaikin, S. Torquato, *Phys. Rev. Lett.* **2004**, *92*, 255506.
[116] A. Simon, W. Bramer, H. J. Deiseroth, *Inorg. Chem.* **1978**, *17*, 875.
[117] D. F. Fredrickson, S. Lee, R. Hoffmann, *Angew. Chem.* **2007**, *119*, 2004; *Angew. Chem. Int. Ed.* **2007**, *46*, 1958.
[118] B. Baranowski, *Pol. J. Chem.* **1992**, *66*, 1737.
[119] M. Hanfland, R. J. Hemley, H-k. Mao, *Phys. Rev. Lett.* **1993**, *70*, 3760.
[120] See also: H.-k. Mao, R. J. Hemley, *Rev. Mod. Phys.* **1994**, *66*, 671.
[121] Z. Soos, D. Mukhopadhyay, *Chem. Phys. Lett.* **1995**, *245*, 194.
[122] B. Edwards, N. W. Ashcroft, *Nature* **1997**, *388*, 652.
[123] If only things were so simple… For a clear analysis of the situation, see: S. G. Wang, Y. X. Qiu, H. Fang, W. H. E. Schwarz, *Chem. Eur. J.* **2006**, *12*, 4101.

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[124] a) A. Jayarama, *Phys. Rev. Lett.* **1972**, *29*, 1674; b) S. Heathman, T. Lebihan, S. Darracq, C. Abraham, D. J. A. Deridder, U. Benedict, K. Mattenberger, O. Vogt, *J. Alloys Compd.* **1995**, *230*, 89.

[125] M. Ross, R. Boehler, P. Soderlind, *Phys. Rev. Lett.* **2005**, *95*, 257801. Including valence d functions in the calculations seems to allow for reasonable reproduction of the fact that the volume change on melting is close to zero (and, thus, of the flatness of the melting curve).

[126] M. Ross, L. H. Yang, R. Boehler, *Phys. Rev. B* **2004**, *70*, 184112.

[127] J. J. Hamlin, V. G. Tissen, J. S. Schilling, *Phys. Rev. B* **2006**, *73*, 094522, and references therein.

[128] a) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **1948**, *76*, 55; b) A. K. McMahan, *Phys. Rev. B* **1984**, *29*, 5982; c) L. J. Parker, T. Atou, J. V. Badding, *Science* **1996**, *273*, 95; d) H. Tups, K. Takemura, K. Syassen, *Phys. Rev. Lett.* **1982**, *49*, 1776.

[129] a) E. Gregoryanz, O. Degtyareva, M. Somayazulu, R. J. Hemley, H.-k. Mao, *Phys. Rev. Lett.* **2005**, *94*, 185502; b) M. Tromel, K. Taxer, *Z. Naturforsch. B* **2005**, *60*, 139.

[130] Perhaps one inspiration for Mendeleev's periodic law was his visit to the ancient Wieliczka salt mines near Krakow in Poland, where he realized that seemingly different compounds such as KCl, NaCl, and NaBr behave and look alike.

[131] In this context, see also the final chapter of: D. A. Young, *Phase Diagrams of the Elements*, University of California Press, Berkeley, **1991**.

[132] Y. W. Fei, J. Li, C. M. Bertka, C. T. Prewitt, *Am. Mineral.* **2000**, *85*, 1830.

[133] Y. W. Fei, C. M. Bertka, L. W. Finger, *Science* **1997**, *275*, 1621.

[134] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H.-k. Mao, R. J. Hemley, *Nat. Mater.* **2004**, *3*, 294. The stoichiometry of the material made has been the subject of substantial discussion: J. von Appen, M. W. Lumey, R. Dronskowski, *Angew. Chem.* **2006**, *118*, 4472; *Angew. Chem. Int. Ed.* **2006**, *45*, 4365; A. E. Young, J. A. Montoya, C. Sanloup, M. Lazzeri, E. Gregoryanz, S. Scandolo, *Phys. Rev. B* **2006**, *73*, 153102, and references therein.

[135] J. C. Crowhurst, A. F. Goncharov, B. Sadigh, C. L. Evans, P. G. Morrall, J. L. Ferreira, A. J. Nelson, *Science* **2006**, *311*, 1275.

[136] A. F. Young, C. Sanloup, E. Gregoryanz, S. Scandolo, R. J. Hemley, H.-k. Mao, *Phys. Rev. Lett.* **2006**, *96*, 155501.

[137] See: E. D. Sloan, Jr., *Nature* **2003**, *426*, 353, and references therein.

[138] a) W. L. Mao, H. K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Z. Guo, J. Z. Hu, J. F. Shu, R. J. Hemley, M. Somayazulu, Y. S. Zhao, *Science* **2002**, *297*, 2247.

[139] Remarkably, alkali halides MX form immiscible metallic melts of M_2X stoichiometry at high pressure and temperature. See, for example: W. Freyland, K. Garbade, H. Heyer, E. Pfeiffer, *J. Phys. Chem.* **1984**, *88*, 3745.

[140] Here, the Au^{I} cation would resemble that in $Au^{I}Cl^{-}$, while the Au^{-} anion would be analogous to that seen in semiconducting $Cs^{I}Au^{-}$: a) W. E. Spicer, A. H. Sommer, J. G. White, *Phys. Rev.* **1959**, *115*, 57. In chemistry, the disproportionation of alkali metals is usually achieved by the use of ligands that can strongly coordinate M^{I} (such as Na^{I}): b) N. C. Pyper, P. P. Edwards, *J. Am. Chem. Soc.* **2000**, *122*, 5092. The proposal here is related to our previous discussion of elemental structures that "disproportionate" at high pressures.

[141] a) A. R. Oganov, M. J. Gillan, G. D. Price, *Phys. Rev. B* **2005**, *71*, 064104. There is evidence for weak O–O bonding in low quartz and in silicates at high pressure: b) G. V. Gibbs, K. M. Rosso, D. M. Teter, M. B. Boisen, M. S. T. Bukowinski, *J. Mol. Struct.* **1999**, *486*, 13; c) G. V. Gibbs, M. B. Boisen, K. M. Rosso, D. M. Teter, M. S. T. Bukowinski, *J. Phys. Chem. B* **2000**, *104*, 10534.

[142] Metallic iron becomes nonmagnetic at a pressure as low as 10 GPa, and superconducting above 15 GPa: K. Shimizu, T. Kimura, S. Furomoto, K. Takeda, K. Kontani, Y. Onuki, K. Amaya, *Nature* **2001**, *412*, 316.

[143] There are cases when even substantial pressure does *not* lead to a major alteration of a particular property of a system. Consider the severely contracted f electrons of the lanthanides: ferromagnetic gadolinium metal with its strong magnetic moment (typical for the $4f^7$ electronic configuration) has been predicted to lose 90% of its magnetic moment only under a 10-fold volume contraction (which corresponds to a pressure of 4000 GPa): Z. P. Yin, W. E. Pickett, www.arXiv.org, cond-mat/0606626v1.

[144] W. Grochala, unpublished results (DFT GGA/PBE calculations; cut-off 300 eV; *k*-point sampling: $6\times6\times6$ for $Ge^{IV}(O^{2-})_2$ (A), $5\times5\times3$ for $Ge^{II}(O_2^{2-})$ (B); ultrasoft pseudopotentials). Cell volume = 63.0 Å^3 (A); 86.2 Å^3 (B). Cell parameters: $a=$ 3.979 Å (A); $a=3.641$, $c=6.506$ Å (B). Charge on oxygen atom: −0.94 e (A); −0.50 e (B).

[145] Y. Song, R. J. Hemley, H.-k. Mao, Z. X. Liu, D. R. Herschbach, *Chem. Phys. Lett.* **2003**, *382*, 686. $[NO]^{+}[NO_3]^{-}$ is here derived from N_2O_4. It can also be made from the application of high pressure to N_2O: M. Somayazulu, A. Madduri, A. F. Goncharov, O. Tscauner, P. F. McMillan, H-k. Mao, R. J. Hemley, *Phys. Rev. Lett.* **2001**, *87*, 135504; C. S. Yoo, V. Iota, H. Cynn, M. Nicol, T. Le Bihan, M. Mezouar, *J. Phys. Chem. B* **2003**, *107*, 5922.

[146] $[NO]^{+}[NO_3]^{-}$ is otherwise known as a pure solid, and in IF_5 solutions: a) L. Parts, J. T. Miller, Jr., *J. Chem. Phys.* **1965**, *43*, 136; b) X. Z. Zhang, K. Seppelt, *Z. Anorg. Allg. Chem.* **1998**, *624*, 667.

[147] C. S. Yoo in *Science and Technology of High Pressure: Proceedings of AIRAPT-17* (Eds.: M. H. Manghnani, W. J. Nellis, M. Nicol), Universities Press, Hyderabad, **2000**, pp. 86–89.

[148] Preliminary results show that La_2WN_4 (in the K_2NiF_4 structure) is stabilized over the system $2\,LaN + WN_2$ by about 2.1 eV per formula unit; W. Grochala, *Pol. J. Chem.*, in press.

[149] M. Tkacz, R. Burtovyy, *Solid State Commun.* **2004**, *132*, 37.

[150] M. I. Eremets, M. Y. Popov, I. A. Trojan, V. N. Denisov, R. Boehler, R. J. Hemley, *J. Chem. Phys.* **2004**, *120*, 10618.

[151] S. Seidel, K. Seppelt, *Science* **2000**, *290*, 117.

[152] a) T. Jaroń, W. Grochala, R. Hoffmann, *J. Mater. Chem.* **2006**, *16*, 1154; b) T. Jaroń, W. Grochala, R. Hoffmann, *J. Molec. Model.*, DOI: 10.1007/s00894-007-0183-x.

[153] 5f electons may be firmly engaged in bonding, as exemplified by the existence of compounds of Th^{IV}, Pa^{V}, U^{VI}, Np^{VII}, and possibly Pu^{VIII}.

[154] There is already evidence for f-orbital involvement in the evolution of f-block intermetallic structures of compositions AB_2 and AB_3: N. V. Chandra Shekar, P. Ch. Sahu, *J. Mater. Sci.* **2006**, *41*, 3207.

[155] Preliminary results show that this comproportionation should happen below 40 GPa: a) D. Kurzydłowski, W. Grochala, unpublished results; b) W. Grochala, *Chem. Soc. Rev.*, in press.

[156] a) C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, M. Bernasconi, M. Parrinello, *Science* **1999**, *283*, 44; b) J.-F. Lin, B. Militzer, V. V. Struzhkin, E. Gregoryantz, R. J. Hemley, H.-k. Mao, *J. Chem. Phys.* **2004**, *121*, 8423; c) A. F. Goncharov, N. Goldman, L. E. Fried, J. C. Crowhurst, I.-F. W. Kuo, C. J. Murphy, J. M. Zaug, *Phys. Rev. Lett.* **2005**, *94*, 125508; d) N. Goldman, L. E. Fried, I.-F. W. Kuo, C. J. Mundy, *Phys. Rev. Lett.* **2005**, *94*, 217801. Ionic conduction has actually been measured for *undoped* water; superionicity has not yet been reached at experimental conditions: E. Katoh, H. Yamawaki, H. Fujihisa, M. Sakashita, K. Aoki, *Science* **2002**, *295*, 1264. The

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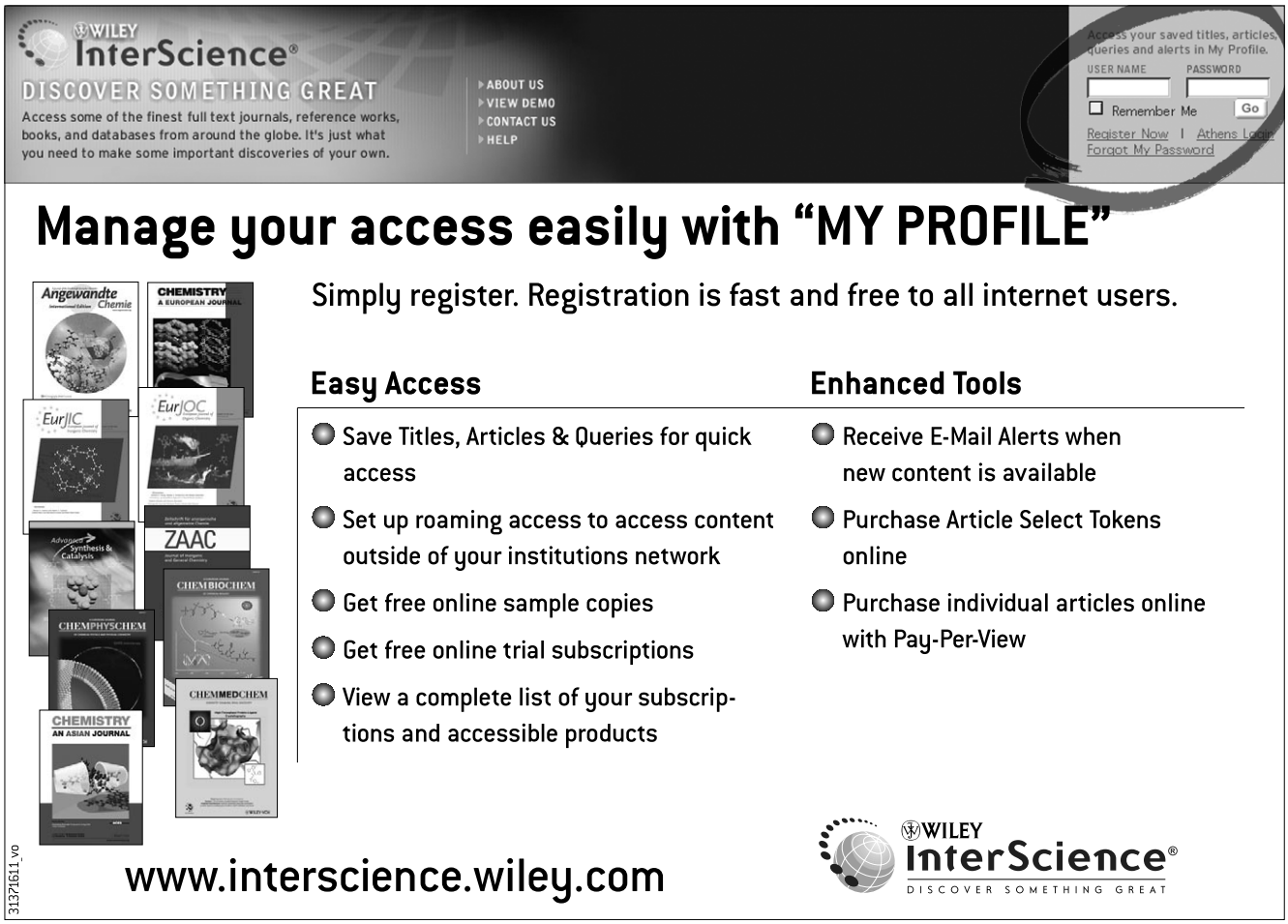
minor doping with HF or NH_3 proposed here should introduce defects and greatly enhance the ionic conductivity of ice.

[157] R. Hoffmann, *Solids and Surfaces, A Chemist's View of Bonding in Extended Structures*, Wiley, New York, **1988**.

[158] When overlap is included in the calculations, the top of the band spreads out to higher energy, and the bottom is compressed. See examples in ref. [157].



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