

Research News

A Theoretical Way of Aiding the Design of Solid-State Syntheses**

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In most areas of chemistry, but especially in organic chemistry, there have developed with time heuristic devices to aid that most fundamental of chemical activities, synthesis. Complete prevision of what will happen in any reaction is not available (except in the hype accompanying computer-aided synthesis programs). But there exists a set of more or less qualitative, eminently useful, chemical notions which guide a chemist along alternative paths to a goal, which often is a thermodynamically unstable but persistent molecule.

In solid-state chemistry the synthetic situation is comparatively dismal. With no disrespect to the multitude of beautiful materials made, and their ingenious makers, we think it is fair to say that at present, a solid-state chemist can *plan* individual synthetic steps only in rudimentary ways. He or she must often rely on 'shake and bake' or 'intelligent guess' techniques; a workable strategy even approximately resembling retrosynthesis^[1] is not available in the field. There is no simple 'Ansatz' to predict non-trivial reaction paths towards *imagined* structures.

One underlying reason for this weakness in synthetic language is that the time-honored and useful concept of acidity and basicity and its associated notions of electrophilicity and nucleophilicity is not well defined in the solid state. The demand for accurate descriptors of reactivity, acidity, and basicity within the solid state is both obvious^[2] and critical.

In the realm of discrete molecules, Pearson's ideas on hard and soft acids and bases^[3] pointed, at first qualitatively, in a new direction. The contribution of Parr and co-workers^[4] has been to quantify the Lewis acid-base concept by means of an accurate quantum-mechanical description of the ground-state properties of finite and infinite molecules, as given within density-functional (DF) theory.^[5] If the total energy E of the ground state is expressed as a power series of the electron number N , a possible small energy change is

given by the chemical potential μ . This equals the slope of the function E versus N at the ground state electron number N^0 . Its negative counterpart, the absolute electronegativity χ , can be approximated by taking the arithmetic average of the ionization potential I and the electron affinity A , as already done earlier in Mulliken's formula [Eq. (1)]. Moreover, the so-called absolute hardness η is proportional to the second derivative of E versus N at N^0 [Eq. (2)] where η describes the curvature of $E(N)$ and measures the electronic tendency of a system to disproportionate and the sensitivity of the electronegativity to a change in the number of electrons. Applied to finite molecules, η can be expressed as shown in Equation 3.

$$\chi \approx \frac{1}{2}(I + A) \quad (1)$$

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{N^0} \quad (2)$$

$$\eta \approx \frac{1}{2}(I - A) \quad (3)$$

This can be seen in Figure 1. For stable systems, η turns out to be a *positive* energy. The higher the absolute hardness, the more *resistant* the chemical species with respect to electronic perturbations. Therefore, inert molecules have large positive η values whereas reactive ones have small positive

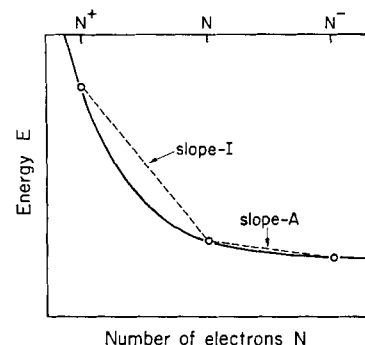


Fig. 1. Total energy E of an atomic or molecular system as a function of the electron number N according to density-functional theory.

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values. A molecule with a negative hardness would decompose into charged pieces.

$$\eta \approx \frac{1}{2}(E^{\oplus} + E^{\ominus}) - E^0 \quad (4)$$

η may be calculated using the three-point finite-difference formula [Eq. (4)] easily applicable to solid-state materials.^[6] Again, η being positive shows that a solid is more likely to stay at E^0 instead of breaking up into two charged pieces having energies of E^{\oplus} and E^{\ominus} . We seek for the specific atomic resistance in the solid towards a global change in the electronic system arising from a chemical attack. The key, we find, is in the ideas of Parr and Pearson on absolute hardness, and their possible consequences for crystal chemistry.^[7]

A recipe for partitioning the absolute hardness into reactivity increments ξ has been presented recently.^[8] One can divide η as shown in Equation (5), where R stands for the atoms within the primitive unit cell used for the electronic structure calculation. The most general description using an energy-resolved k -averaged (spectral) density-of-states matrix (restricted to the non-spin-polarized case here) reveals that the total electronic energy (equal to the total energy within an extended Hückel theory^[9]) is given by Equation (6) where μ and ν are the atomic orbitals in the LCAO formalism, and the abbreviations h and $P(\epsilon)$ stand for the one-electron Hamiltonian matrix elements (potentially energy-dependent) and the density-of-states matrix, respectively. \Re characterizes the real parts of the complex off-diagonal entries in $P(\epsilon)$.

$$\eta \equiv \sum_R \xi_R \quad (5)$$

Using some minor simplifications that suppress the (small) electronic relaxation of deep-lying levels (i.e. assuming a 'frozen band' approximation, the solid-state analogue of Koopmans' theorem^[10]), a simplified gross atomic reactivity increment ξ_R may be written as shown in Equation (7).

The off-diagonal term [second line in Eq. (7)] represents the important energy (hardness) changes due to atomic interaction. It is useful, in fact, to focus attention on this bonding term by defining a corresponding bond increment [Eq. (8)].

$$E = \sum_R \sum_{\mu \in R} \left\{ \int_{\epsilon_p^0}^{\epsilon_F} h_{\mu\mu} P_{\mu\mu}(\epsilon) d\epsilon + \sum_{R'} \sum_{\nu \in R'} \int_{\epsilon_p^0}^{\epsilon_F} h_{\mu\nu} \Re [P_{\mu\nu}(\epsilon)] d\epsilon \right\} \quad (6)$$

$$\xi_R \approx \frac{1}{2} \sum_{\mu \in R} \left\{ h_{\mu\mu} \left(\int_{\epsilon_p^{\oplus}}^{\epsilon_p^{\ominus}} P_{\mu\mu}(\epsilon) d\epsilon - \int_{\epsilon_p^{\oplus}}^{\epsilon_p^0} P_{\mu\mu}(\epsilon) d\epsilon \right) + \sum_{R'} \sum_{\nu \in R'} h_{\mu\nu} \left(\int_{\epsilon_p^{\oplus}}^{\epsilon_p^{\ominus}} \Re [P_{\mu\nu}(\epsilon)] d\epsilon - \int_{\epsilon_p^{\oplus}}^{\epsilon_p^0} \Re [P_{\mu\nu}(\epsilon)] d\epsilon \right) \right\} \quad (7)$$

$$\xi_{RR', \text{bond}} \approx \frac{1}{2} \sum_{\mu \in R} \sum_{\nu \in R'} h_{\mu\nu} \left(\int_{\epsilon_p^{\oplus}}^{\epsilon_p^{\ominus}} \Re [P_{\mu\nu}(\epsilon)] d\epsilon - \int_{\epsilon_p^{\oplus}}^{\epsilon_p^0} \Re [P_{\mu\nu}(\epsilon)] d\epsilon \right) \quad (8)$$

The ϵ_F s represent the slightly varying Fermi energies up to which the integrations have to be carried out (up to ϵ_F^{\oplus} for the $N-1$ case, for instance) in order to give the total electronic energies.^[11]

A visualization of the atomic increments may be found in Figure 2, where a highly schematic E versus N representation

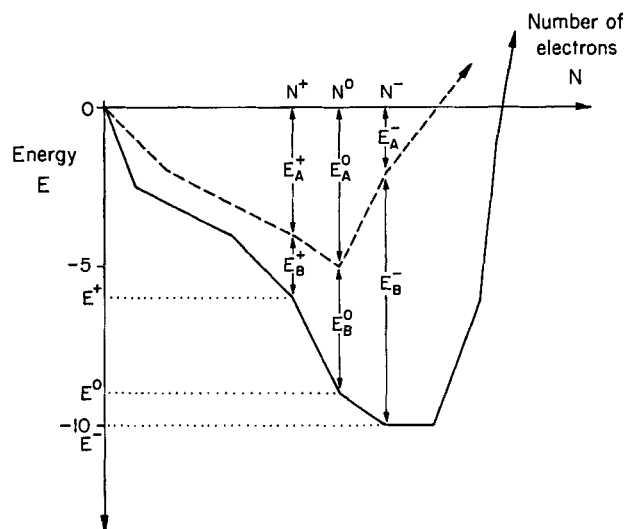


Fig. 2. Scheme of the total energy partitioning and its relationship with gross atomic increments of reactivity, electrophilicity, and nucleophilicity. The lower curve (solid line) represents the course of the total energy (left axis, arbitrary units) as a function of the electron number (right axis) of a solid-state material AB composed of two different atoms A and B. The total energies E^{\oplus} , E^0 , E^{\ominus} belonging to electron numbers N^{\oplus} , N^0 , N^{\ominus} are emphasized. The upper curve (broken line) divides the total energy into contributions of atom A (upper region) and atom B (lower regions), i.e. into their atomic energies $E_{A,B}^{\oplus}$, $E_{A,B}^0$, and $E_{A,B}^{\ominus}$.

for a solid-state material composed of two atoms, say A and B, is shown. The solid curve represents the total energy of AB. It has an absolute hardness of $\eta \approx \frac{1}{2}(E^{\oplus} + E^{\ominus}) - E^0 = \frac{1}{2}(-6 - 10) + 9 = 1$ (in arbitrary energy units) which is positive since AB is chosen to be stable. The broken line separates the atomic energies of atom A (upper part) and atom B (lower part) from each other. For each N , they add up to the total energy of AB. Assuming a 'frozen band' picture, the gross reactivity increments are $\xi_A = \frac{1}{2}(-4 - 2) + 5 = 2$ and $\xi_B = \frac{1}{2}(-2 - 8) + 4 = -1$, which means that atom B is more reactive than atom A, as B has the lower increment, decreasing the absolute hardness. Both increments add up to the total hardness, $\xi_A + \xi_B = 2 - 1 = 1 = \eta$.

One way of probing the acid-base behavior of a crystal would be to look at its initial energy perturbations upon reaction while focusing on an arbitrary interaction with a nucleophilic (electrophilic) reagent where the crystal reacts as an electrophile (nucleophile) by accepting (donating) partial charge. Then there will be an electrophilic energy change $\Delta E^{\text{e}^{\ominus}}$ [Eq. (9)] and a nucleophilic energy change $\Delta E^{\text{n}^{\oplus}}$ [Eq. (10)] both composed of atomic subcontributions. In

Figure 2 we have $\Delta E^{\text{ele}} = -10 + 9 = -1$ and $\Delta E^{\text{nuc}} = -6 + 9 = 3$ (arbitrary energy units).

$$\Delta E^{\text{ele}} \approx E^{\ominus} - E^0 \equiv \sum_R \xi_R^{\text{ele}} \quad (9)$$

$$\Delta E^{\text{nuc}} \approx E^{\oplus} - E^0 \equiv \sum_R \xi_R^{\text{nuc}} \quad (10)$$

The energy perturbations can be partitioned into a set of atomic (or bond) increments for electrophilicity and nucleophilicity.^[8] For example, a simplified gross atomic electrophilicity increment $\tilde{\xi}_R^{\text{ele}}$ can be expressed as shown in Equation (11), whereas a bond electrophilicity increment is given by Equation (12).

$$\tilde{\xi}_R^{\text{ele}} = \sum_{\mu \in R} \left\{ h_{\mu\mu} \int_{\epsilon_F^{\ominus}}^{\epsilon_F^0} P_{\mu\mu}(\epsilon) d\epsilon + \sum_{R'} \sum_{\nu \in R'} h_{\mu\nu} \int_{\epsilon_F^{\ominus}}^{\epsilon_F^0} \Re[P_{\mu\nu}(\epsilon)] d\epsilon \right\} \quad (11)$$

$$\tilde{\xi}_{RR', \text{bond}}^{\text{ele}} = \sum_{\mu \in R} \sum_{\nu \in R'} h_{\mu\nu} \int_{\epsilon_F^{\ominus}}^{\epsilon_F^0} \Re[P_{\mu\nu}(\epsilon)] d\epsilon \quad (12)$$

The definitions for the corresponding nucleophilicity increments can be obtained from the electrophilic ones simply by replacing the varying Fermi energy ϵ_F^{\ominus} by ϵ_F^{\oplus} .

For the electrophilicity increments in Figure 2 we arrive at $\tilde{\xi}_A^{\text{ele}} = -2 + 5 = 3$ and $\tilde{\xi}_B^{\text{ele}} = -8 + 4 = -4$. So B is the more acidic atom since it has the lower increment. The increments of nucleophilicity are $\tilde{\xi}_A^{\text{nuc}} = -4 + 5 = 1$ and $\tilde{\xi}_B^{\text{nuc}} = -2 + 4 = 2$, stating that A is the more basic atom. Both kind of increments add up to the corresponding energy changes, i.e. $\tilde{\xi}_A^{\text{ele}} + \tilde{\xi}_B^{\text{ele}} = 3 - 4 = -1 = \Delta E^{\text{ele}}$ and $\tilde{\xi}_A^{\text{nuc}} + \tilde{\xi}_B^{\text{nuc}} = 1 + 2 = 3 = \Delta E^{\text{nuc}}$.

The absolute hardness is the average of the acid–base perturbation energies [Eq. (13)] which can be illustrated in Figure 2 as $\eta \approx \frac{1}{2}(\Delta E^{\text{ele}} + \Delta E^{\text{nuc}}) = \frac{1}{2}(-1 + 3) = 1$. Consequently, a similar relationship holds for increments of reactivity, electrophilicity, and nucleophilicity [Eq. (14)] for the atoms and for the bonds [Eq. (15)]. Thus, reactivity is linked with both acid and base behavior, suggesting the reactivity increment is in reality a kind of ‘amphoteric’ value.

$$\eta = \frac{1}{2}(\Delta E^{\text{ele}} + \Delta E^{\text{nuc}}) \quad (13)$$

$$\xi_R = \frac{1}{2}(\xi_R^{\text{ele}} + \xi_R^{\text{nuc}}) \quad (14)$$

$$\xi_{RR', \text{bond}} = \frac{1}{2}(\xi_{RR', \text{bond}}^{\text{ele}} + \xi_{RR', \text{bond}}^{\text{nuc}}) \quad (15)$$

Can a chemical bond be ‘acidic’ or must it always be ‘basic’ as it has electrons in it? In general, the latter is *not* the case, at least not in the way we look at the problem.^[12] Indeed, if the interaction of two atoms leads to high-lying, occupied *and* antibonding levels, the bonding of these two

atoms will be basic in nature, for their electronic interaction will become stronger by releasing (donating) electrons, depopulating antibonding states.

This matches our preconceptions. But what is an acidic bond? With our definitions it is a pair of atoms which accepts electrons readily, i.e. the molecule has low-lying unoccupied states with bonding character in the bond specified, making it a good electron acceptor.

The sense in which the word ‘bond’ is used here is a little different from the usual conception. It refers to a pair-wise partitioning of the total energy of the molecule or solid or what RR' contributes to the total energy.^[13] There is no implication that there is precisely one pair of electrons shared between R and R' . The bonding situation between R and R' might be electron-poor, electron-precise, or electron-rich.

The lower the increments (which are defined as energy values measured in eV) the higher the reactivity, acidity, or basicity.^[14] A highly reactive (acidic, basic) atom or bond is detected from a large associated *negative* increment of reactivity (electrophilicity, nucleophilicity). On the contrary, an atom or bond showing no sign of reactivity (acidity, basicity) is characterized by a large *positive* increment of reactivity (electrophilicity, nucleophilicity). Figure 3 graphically summarizes the trends.

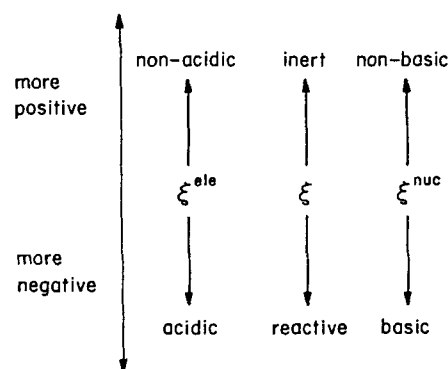


Fig. 3. Interpretational help for the increments of reactivity, electrophilicity and nucleophilicity.

With the help of these increments it is possible, in principle, to characterize local spatial regions within a crystal structure as possible targets for electrophilic or nucleophilic attack. Here are two vivid examples illustrating use of the reactivity–acidity–basicity description of atoms and bonds within the solid state:

The topochemical transformation of $K_2Ti_4O_9$ into $K_2Ti_8O_{17}$ is a representative acid–base reaction of a layered solid-state material.^[15] The sheet structure of $K_2Ti_4O_9$ (Fig. 4) contains zigzag Ti–O structural units formed from four edge-sharing TiO_6 octahedra, connected to neighboring entities by sharing corner O atoms. A single Ti–O unit is also linked by common edges with similar blocks above and below. K^{\oplus} ions, located in channel-like voids, can be complete-

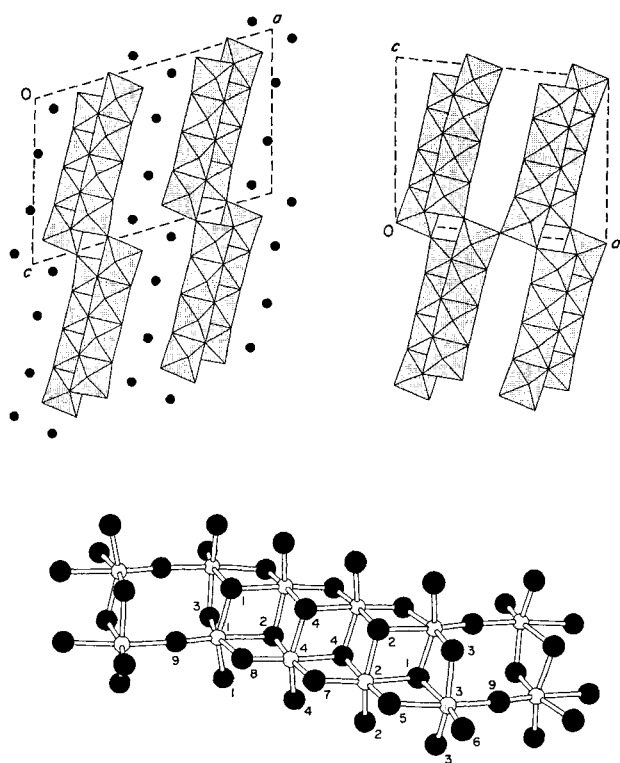


Fig. 4. Top) Projection of the crystal structures of $K_2Ti_4O_9$ along the [010] direction (left) and of $K_2Ti_8O_{17}$ along the [010] direction (right). The Ti-O substructure is represented with shaded octahedra, and the K atoms are given as black circles (omitted for clarity in the right picture). The edges of the unit cell are emphasized with broken lines. Bottom) Perspective view of the Ti-O substructure of $K_2Ti_4O_9$, approximately along the [100] direction. The Ti atoms are given as small open circles and the O atoms as large bold circles.

ly exchanged by H_3O^+ ions upon treating $K_2Ti_4O_9$ with 3N nitric acid at room temperature. Heating the hydrolysis product leads to water emission, accompanied by internal protonation of the oxygen atoms, forming OH groups facing each other. Even higher temperatures result in further H_2O elimination, and finally neighboring Ti-O polyhedral blocks are sealed to form the $K_2Ti_8O_{17}$ structure (Fig. 4). The hydrolysis does not destroy the basic framework, and the only change lies in the additional linking of the Ti-O ribbons by a shared angular O atom.

It has been argued^[2] that the mechanism of this reaction is based on a selective protonation of sites according to their basicities. The angular oxygen atoms represent the most basic sites which are to be protonated. We have calculated the internal basicities within the material,^[8] and we have furthermore investigated the change in basicity of the angular O atom upon exchanging one Ti^{4+} ion by an Nb^{5+} , keeping the same geometry.

The total energy calculations are in perfect accord with Pearson's maximum hardness principle. The electronic resistance of the neutral $K_2Ti_4O_9$ phase is highest (about 2.55 eV), and more than twenty times larger than any charged (electronically perturbed) species. Quantum mechanics has optimized all electronic interactions for the neutral electron

count in order to separate stabilizing and destabilizing states from each other as far as possible. The calculations indicate that $K_2Ti_4O_9$ is an electronic insulator, in agreement with recent electrical studies.^[16] The small hardness value of the hypothetical Nb-substituted compound " $K_2NbTi_3O_9$ " (about 0.13 eV) indicates a truly greater reactivity because of its internal electronic perturbation.

The reactivity increments (see [8] for numerical details) show that the Ti(3) atom, located at the 'end' of the condensed octahedra (Fig. 4), is the most reactive, according to $Ti(3) \gg Ti(1) > Ti(2) > Ti(4)$.

The most reactive O atoms lie around Ti(3). Obviously, the last of the condensed Ti-O octahedra forms an island of reactivity. Comparatively unreactive O atoms such as O(2) and O(4) are 'buried' in the very middle of the polyhedral framework. For the case of " $K_2NbTi_3O_9$ " where an Nb atom replaces the Ti(3) atom, the metals' reactivities have changed remarkably to $Ti(1) \geq Ti(4) \geq Ti(2) \gg Nb$.

It is also noticeable that the reactivities of the O atoms (except O(3)), quite different in $K_2Ti_4O_9$, have been smoothed, no great diversities remaining. The influence of the single Nb atom on the reactivities is astonishing.

How about acidity in a compound whose primary chemical character is basic? It's not very surprising that the computed atomic electrophilicities are quite small, especially for the O atoms; they are not 'acidic'. Only the Ti(3) atom is more electrophilic; so again the 'corner' atom stands out. Concerning the acidity of the atoms in " $K_2NbTi_3O_9$ ", the situation is even more extreme than before. O acidities have decreased even more, and the acidity of this phase is totally based on the Nb atom—in perfect agreement with chemical intuition! Surely, a formal Nb(v) atom represents a stronger Lewis acid compared to a Ti(IV) atom, and we may expect the Nb atom to be the weakest Lewis base in this hypothetical structure.

The compound's most interesting feature is its basicity. In $K_2Ti_4O_9$ all atomic nucleophilicities indicate truly basic behavior. Regarding the Ti atoms, the rank of basicities is very homogenous, in the sense that no Ti atom is exceptional. The most distinct differences in basicity emerge at the O atoms which lie at the reacting internal surface. The order is $O(6) > O(3) > O(9) > O(5) > O(1) > O(7) > O(8) \gg O(2) \gg O(4)$, being the same as the one in the reactivity section, a clear hint that the O atom reactivities run parallel to their basicities! We stress that the most basic O atoms, namely O(6), O(3), O(9), O(5), and O(1) are the atoms surrounding the most reactive (and most acidic) Ti atom at the corner octahedron. Specifically, it is the O(6) atom which is protonated in the solid-state acid-base reaction.^[17]

To form even higher condensates, further protonation of the O atoms at the 'long edge' should take place. Indeed, the basicity scale shows a continuous decrease along O(6), O(5), O(7), and O(8). On the contrary, the least basic (and least reactive) atoms O(2) and O(4) are never affected in these reactions. They are located in the inner part of the Ti-O framework and their nucleophilicity is extremely small.

Within “ $\text{K}_2\text{NbTi}_3\text{O}_9$ ”, the expected diminished basicity of the Nb atom is confirmed. According to $\text{Ti}(4) \geq \text{Ti}(2) > \text{Ti}(1) \gg \text{Nb}$, the former order of the Ti atoms is inverted, transforming the inner Ti atoms into the more basic and the outer atoms into the less basic ones. The strong Lewis acid Nb(v) represents the least basic site. Looking at the basicities of the O atoms, $\text{O}(4) \approx \text{O}(7) \geq \text{O}(8) \geq \text{O}(2) > \text{O}(1) > \text{O}(6) > \text{O}(9) \geq \text{O}(5) > \text{O}(3)$, O(6) and other O atoms at the end of the Ti–O entity have been greatly reduced in basicity and the centers of basicity are now located mainly in the middle of the building block! In chemical language, this is the result of an extremely strong acid’s (Nb(v)) power to weaken the basicity of its environment.

Why such drastic changes upon Nb substitution? Three reasons occur to us: First, the influence of the different spa-

tial extent of the atomic wave functions, such as those of the Ti atom are more ‘diffuse’ than for Nb. Second, the differences in electronegativity have some influence on the order of the basicities of the O atoms. Third, there is simply the perturbation from the additional electron introduced by Nb substitution. Numerical experiments indicate that the last factor, the extra electron which enters an antibonding band, is responsible for the dramatic change in reactivity and basicity.

A second application: The family of compounds AMo_3X_3 (A = electropositive metal of main group I, II, or III; X = chalcogenide) is remarkable both for its structural and physical properties.^[18] Its structure (Fig. 5) may be described as a linear condensation of an infinite number of face-sharing Mo_6X_8 octahedra,^[19] thereby forming one-dimensional $(\text{Mo}_{6/2})_{\infty}^1$ metal chains, surrounded by X atoms and isolated from each other by A atoms.

It was shown that AMo_3X_3 compounds containing Li, Na on the one hand and Se, Te on the other can be dissolved in highly polar solvents, forming very long, solvated Mo_3Se_3 strings as well as solvated A ions.^[20] Interestingly, solubility behavior differs from one compound to another: Li com-

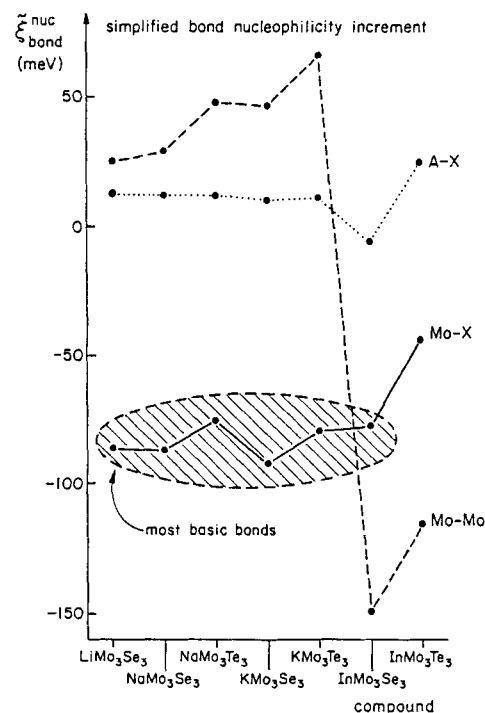
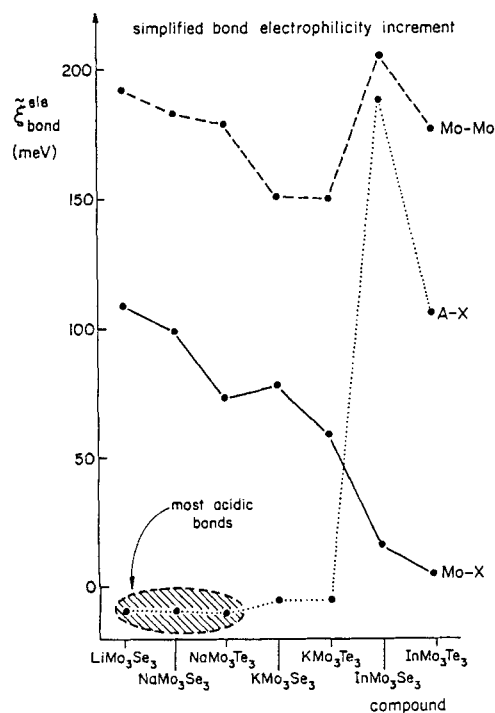
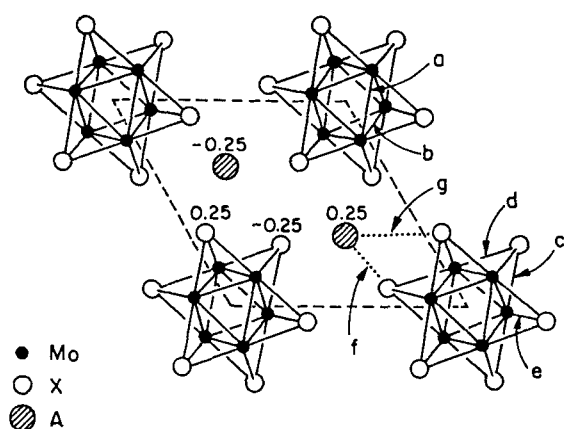


Fig. 5. Top) Projection of the crystal structure of AMo_3X_3 phases along the hexagonal axis. Mo atoms, given as small, filled circles, are bonded to surrounding X atoms, drawn as open, medium-sized circles. Electropositive A atoms, given as large, shaded circles, lie within the central tunnel of the structure. The letters a to g label the bonds. Bottom) Outline of the average Mo–Mo, Mo–X, and A–X simplified bond electrophilicity increments (left) and simplified bond nucleophilicity increments (right) in AMo_3X_3 phases.

pounds are easily dissolved, Na compounds are only partially (colloidally) soluble, whereas pure K or In compounds are not soluble at all.

As far as the solvent is concerned, its dielectric constant ϵ might be thought to help in judging whether the solid will dissolve. A fact that has been overlooked, however, is that all 'good' solvents represent strong Lewis bases. By looking at one empirical measure of Lewis basicity, such as Gutmann's donor numbers DN,^[21] the hierarchy of dissolving power is indeed well correlated. But why i) is the AMo_3X_3 structure decomposed into 'Mo₃Se₃' and 'A' species and ii) why are there such striking differences between compounds containing different electropositive metal atoms? Despite the implications of Figure 5 (no "bonds" between X and A, "bonds" between Mo and X atoms), it is not clear at the outset which parts of the structure will be disconnected or which will remain intact. One could have imagined further decomposition, breaking Mo–Mo bonds, to Mo₃ or even smaller units.

Keeping the solvent basicities in mind, besides solvation/lattice energy competitions, the reactivities, acidities, and basicities of the bonds strongly influence the solvation and disconnection behavior. It can be shown^[22] that all 'good' solvents (Lewis bases) attack the most acidic bonds within the structure type first, decomposing the structure at spatial regions of high acidity.

Although Figure 5 is drawn in accordance with an inorganic chemist's bonding intuition, could there be validity in a different representation, where the main emphasis is put onto the A–X bonds, for example? Could a possible decomposition of the structure into 'Mo' and 'A–X' fragments also be realized?

In Figure 5, there are seven different internuclear distance types, where a and b are Mo–Mo, c to e are Mo–X and f and g are A–X bonds. Based on their multiplicities, one may calculate characteristic observables (bond energies, increments etc.) in order to treat the Mo–Mo, Mo–X, and A–X bonding substructures as separate entities. The result of the bond-length analysis is that Mo–Mo bonding is not strongly influenced by changes in the A and X composition. All Mo–X and A–X bond lengths show a characteristic zigzag pattern between the Se and Te compounds, corresponding to the difference in Pauling covalent radii.

The total energy calculations reveal the 'softening' of the compounds' electronic resistances in going from LiMo_3Se_3 to InMo_3Te_3 ; the absolute hardness η decreases continuously from 0.43 to 0.10 eV. This may be explained by the intensification of covalent bonding along the series Li, Na, K, and In. Consequently, the Te compounds are always less 'hard' than the Se compound. Concerning bond energies, smooth curves appear both for the Mo–Mo bonds as well as for the about 1.5 times 'stronger' Mo–X bonds. For the A–X bonds, however, a sharp decrease in bond energy is found for the K case. This unexpected finding, showing the local geometry to be most unfavorable for the relatively larger K cations, cannot be well correlated with the solubility behavior! The stronger A–X bonds (Li–Se, Na–Se, Na–Te) are broken

whereas the weaker (K–Se, K–Te) remain intact. But what is the reason for the difference in solubility?

Average values for simplified bond reactivity increments (amphoteric descriptors) reveal that the Mo–Mo bonds are the least reactive bonds within the structure, rather insensitive to varying electronic conditions. This fact is of major importance for the survival of the 'X-wrapped' infinite Mo string during its reaction with the polar solvents. On the contrary, both Mo–X as well as A–X bonds have small positive or even negative reactivity increments. They form the reactive internal regions of the structure. Thus, the reactivity increments give a totally different description of the structure.

To elucidate the solubility behavior, the 'amphoteric' reactivity increments were broken down into increments of electrophilicity and nucleophilicity. Averaged values for the simplified bond electrophilicity increments are given in Figure 5, revealing a large heterogeneity in acidic character. First, the Mo–Mo bonds are not acidic at all since they always have highly positive increments. Second, the Mo–X bonds display a nearly continuous increase in acidity in going from the Li phase to the In phases, although they do not represent the most acidic bonds. These are, indeed, the A–X bonds that incorporate Li, Na, K on the one side and Se, Te on the other. Such local 'islands of acidity' must have a strong tendency to react with Lewis bases—in perfect agreement with the solution experiments!

Thus the event of solvation (of this and we believe most other dissolutions) is started by a solid-state liquid-state donor–acceptor acid–base reaction. The A–X bonds represent the 'targets' for the nucleophilic solvents. To be more quantitative, the dissolvable Li and Na compounds have the largest negative A–X bond electrophilicity increments. The values of the K compounds seem to appear a bit too negative, for KMo_3Se_3 and KMo_3Te_3 cannot be brought into solution. This might be a sign that the extended Hückel parameters for K need further modification.

We believe that an alternative mode of fragmentation in solution may exist. Averaged simplified bond nucleophilicity increments are shown in Figure 5. The basicity of the Mo–Mo bonds is still the weakest of all. Likewise, the A–X bonds appear to be hardly basic—of course they cannot be so, as they proved to be the most acidic.^[23] But all Mo–X bond nucleophilicity increments are strongly negative, indicating these bonds are highly basic. We propose that these 'islands of basicity' should be easily attacked by Lewis acids. Such solvents should both have a high acceptor number AN (strong acidity) and a high dielectric constant (giving rise to a high solvation energy). Probably trifluoromethanesulfonic acid $\text{CF}_3\text{SO}_3\text{H}$ ($\text{AN} \approx 129.1$) or antimony pentachloride in 1,2-dichloroethane ($\text{AN} \approx 100.0$) would be good candidates for luring the infinite Mo string out of its wrapping by X atoms. Although the detailed calculation of a real solvation process lies beyond our present approach, we stress that the Mo–X bonds are reasonable targets for acidic solvents, and they will be attacked first. Such a hypothesis cannot be ex-

tracted from the 'static' graphical representation of the structure of Figure 5.

Our investigation is in accord with the typical graphical bonding presentation and chemical preconceptions (bond-energy order) of these compounds. But we also access reactivity, where only Mo–X and A–X bonds but not Mo–Mo bonds (highly inert) stand out. Breaking the reactivity up into acidity and basicity, the solubility behavior is rationalized in terms of the A–X bonds' strong acidities. The highly basic character of Mo–X bonds gives rise to the hypothesis that these bonds could be attacked by acidic solvents, eventually releasing a purely metallic chain, probably condensing to form colloidal metal particles. The typical graphical representation of a solid-state compound should not be indiscriminately used as a predictor of reactivity, because the latter depends on the reaction type.

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Research News

Disordered Stripe Domain Phases in Two Dimensions: “Labyrinths” and “Stripe Liquids” in Magnetic and Organic Thin Films

By Michael Seul*

1. Introduction to Modulated Phases

In many diverse condensed-matter systems, competing interactions stabilize modulated phases in which the pertinent order parameter field exhibits periodic spatial variations, uni-directionally modulated “stripe” and trigonally modulated “bubble” phases generally representing the simplest configurations. The modulation period is determined by the balance of competing contributions to the free energy and generally varies as a function of temperature and applied field(s).^[1] The generic scenario involves a repulsive interaction of long range whose preference for continued subdivision of domains, or regions characterized by a uniform amplitude of the order parameter, is balanced by the free-energy

cost incurred in the creation of “domain walls”. In a surprising number of instances, the formation of domain patterns and their evolution in response to variations in experimental parameters may be understood on the basis of this simple picture. This includes the occurrence of such phenomena in systems as diverse as ferroelectrics, layers of ferromagnetic colloids (“ferrofluids”) and thin slabs of type-I superconductors, as well as thin ferrimagnetic garnet films and amphiphilic (“Langmuir”) monolayers confined to an air–water interface.^[2]

Domain shapes and patterns in the latter two, effectively two-dimensional systems have been recently examined in detail, relying on a combination of optical microscopy and extensive digital image analysis.^[3–5] Domain formation in magnetic films arises from the presence of (sample-shape dependent) demagnetizing fields. For thin plates, these have been modeled in the form of a repulsive dipolar interaction which is balanced by the attractive exchange interaction be-

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