

plating with microelectrodes. Complex circuit paths could be formed by etching through a conducting layer deposited on an insulating substrate. The virtue of the piezoelectric micromanipulator in this application lies in the fact that it is controlled by electrical signals. These could be recorded on magnetic tape while a given operation is being performed manually, then played back through the operating head to repeat the operation. With these techniques, complex circuits of unprecedentedly small size could be fabricated automatically. If such a scheme should prove feasible, the microcircuits produced could, in turn, have important applications in biomedical research.

References and Notes

1. J. H. Emerson, U.S. Patent No. 1,828,460 (1931).
2. P. de Fonbrune, *Compt. Rend.* **195**, 603 (1932).
3. M. Cailloux, *Rev. Can. Biol.* **25**, 528 (1943).
4. J. M. Mitchison, *J. Exptl. Biol.* **30**, 515 (1953).
5. A. Tyler and A. Monroy, *Biol. Bull.* **109**, 307 (1955).
6. J. E. Pascoe, *J. Physiol. (London)* **128**, 26P (1955).
7. V. Bush, W. R. Duryee, J. A. Hastings, *Rev. Sci. Instr.* **247**, 487 (1953).
8. L. A. Petermann, *Elec. Mfg.* **1955**, 99 (Dec. 1955).
9. G. W. Ellis, thesis, Univ. of California, Berkeley (1961).
10. K. S. Lion, *Instrumentation in Scientific Research—Electrical Input Transducers* (McGraw-Hill, New York, 1959).
11. J. Curie and P. Curie, *Bull. Soc. Min. France* **3**, 90 (1880).
12. G. Lippmann, *Compt. Rend.* **92**, 1049, 1149 (1881).
13. J. Valasek, *Phys. Rev.* **17**, 475 (1921).
14. Pierre Curie was also the discoverer of the temperature-dependent transition of ferro-

- magnetic substances to paramagnetic substances, although he did not, in his piezoelectric studies, observe this change from ferroelectric to paraelectric states.
15. C. B. Sawyer and C. H. Tower, *Phys. Rev.* **35**, 269 (1930).
16. C. B. Sawyer, *Proc. I.R.E. (Inst. Radio Engrs.)* **19**, 220 (1931).
17. Bimorph is a trade name applied, by Sawyer's employer, Brush Laboratories, to the transducers he developed.
18. W. Jackson and W. Reddish, *Nature* **156**, 717 (1945).
19. The transducer is model CRIA, manufactured by the American Microphone Company, Pasadena, Calif.
20. The transducer is model X-26, manufactured by the Astatic Corporation, Conneaut, Ohio.
21. W. G. Cady, *Piezoelectricity* (McGraw-Hill, New York, 1946), pp. 547-548.
22. The work on the effects of mechanical injury to the cell nucleus and part of the work on the satellite micromanipulators was supported by U.S. Public Health Service grant No. RC-6025; Daniel Mazia was the principal investigator. This article is based on work done when I was a graduate student under Professor Mazia in the zoology department of the University of California, Berkeley.

Molecular Designing of Materials

Science, guided by molecular understanding, takes up
the challenge to create materials for the future.

Arthur R. von Hippel

Exploration of the resources of our planet, only a generation ago still left to the individual prospector, geologist, or mining engineer, is now a joint concern of the scientific world community, as the recent International Geophysical Year testifies. Our present knowledge of mineral resources has been summarized with penetrating understanding by Meyerhoff (1). How to sustain an explosively growing world population is the theme of pioneering studies like those of Harrison Brown (2). Catastrophe will be the assured outcome of this situation if political and economic

insight cannot win the race against prejudice and ignorance. It is the unhappy fate of the scientist today that he must play the role of Cassandra in the body politic, sending his fellow men to bed with nightmares in the hope of being heard in time.

Fortunately, an article on the molecular designing of materials need not be gloomy; on the contrary, I want to report on developments bright with promise, starting with the apparently naive question: What shall we most reasonably do with our natural resources? In earlier times the answer was simple: Here are the materials found in nature and transformed by industry; there are their macroscopic properties, defined and tabulated. Add the practical experience of the engineer and the economic incentive of maxi-

mum profit. Into this mold our demands had to fit, rudely deprived of soaring imagination.

Suddenly all this is changing. "Molecular science"—in decades of quiet studies on electrons, atoms, molecules, and their concerted action in gases, liquids, and solids—has made a more powerful approach possible: "molecular engineering," the building of materials and devices to order. We begin to design materials with prescribed properties, to understand the molecular causes of their failings, to build into them safeguards against such failure, and to arrive at true yardsticks of ultimate performance. No longer shackled to presently available materials and characteristics, we are free to dream and find answers to unprecedented challenges. Simultaneously we begin to foresee, in ever-widening perspective, the consequences of our actions. It is about this revolutionary situation, which makes scientists and engineers true allies in a great adventure of the human mind, that I am going to speak (3), though fully aware that most facts here presented are well known to the specialist and that I need your indulgence for trying to unfold a great panorama despite limited insight.

The Web of Electron Clouds

When an ultimate Power created protons and electrons, the basic building laws for this world were decided. The two particle types, equipped with equal but opposite elementary electric

The author is professor of electrical engineering at the Massachusetts Institute of Technology, Cambridge, and director of the Institute's Laboratory for Insulation Research. This article is the lecture which he delivered on 26 December 1961 at the Denver meeting of the AAAS, at the general session, "The Moving Frontiers of Science."

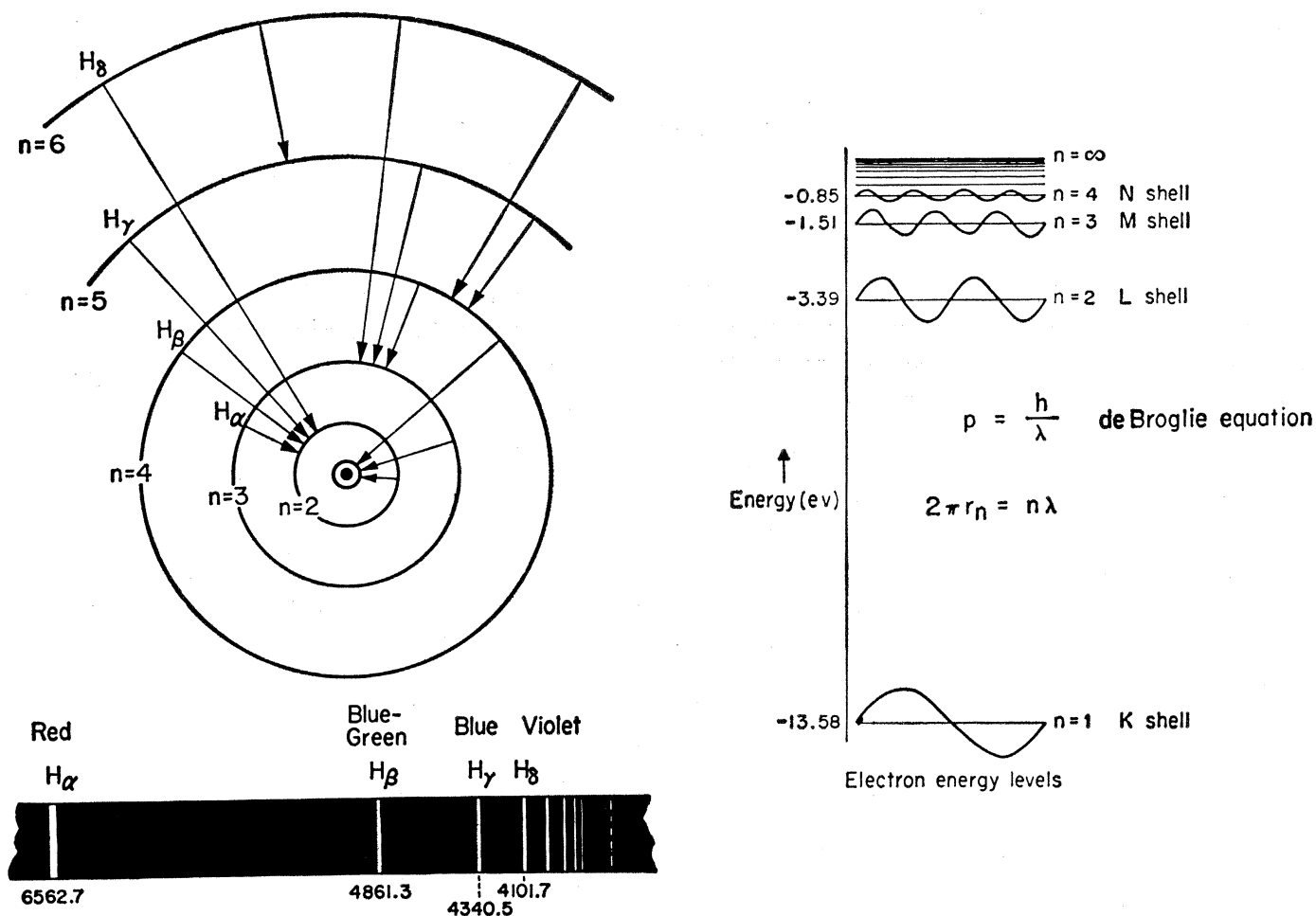


Fig. 1. Standing-wave modes and Bohr orbits of the hydrogen atom.

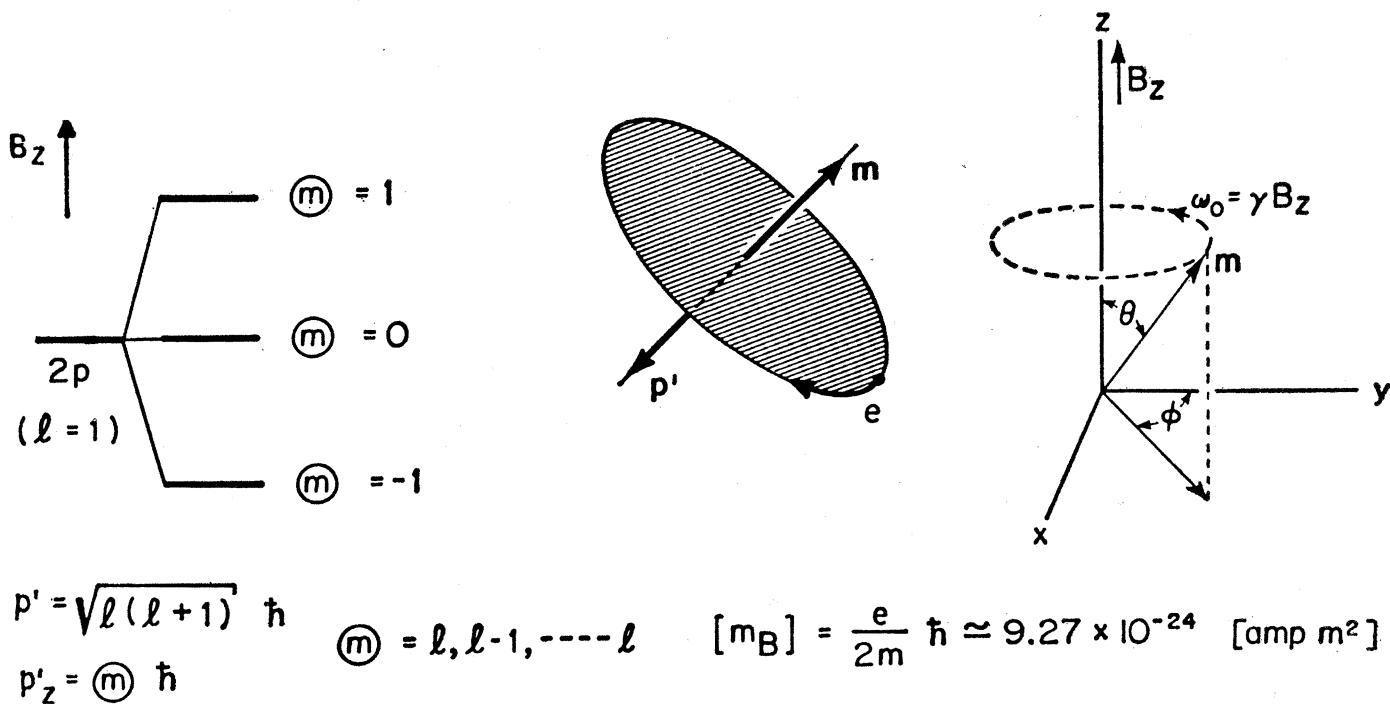


Fig. 2. Orbital electron as a gyroscope.

charges, can hold and neutralize each other electrostatically. However, not only do their masses exercise gravitational action of the same sign, thus offering no shield against gravitational forces, but the proton is heavier by three orders of magnitude ($m_+/m_- \approx 1836$). This fact has profound consequences.

The accuracy with which particles can be localized, in our space-time framework, is proportional to their mass (the Heisenberg uncertainty relation). In wave-mechanical language, the wavelength of a particle is inversely proportional to its momentum, hence its mass. The probable whereabouts of particles in stationary states can be described by standing-wave modes of these de Broglie probability waves as solutions of Schrödinger's wave equation (Fig. 1). An electron trapped by the Coulomb field of a proton in its lowest energy state is with greatest probability found in a circular Bohr orbit whose circumference equals one wavelength; hence, its radius is inversely proportional to the electron mass. As for any satellite circling the earth, this orbit must have mechanical stability—that is, the attraction force of the nucleus and the centrifugal force must balance. Thus, its average radius for an electron trapped by a proton in its ground state can be calculated as $r_0 \approx 5.28 \times 10^{-11}[m]$, while for the proton the corresponding radius would be about 1836 times smaller, or about $3 \times 10^{-14}[m]$. At such small distances, nuclear attraction forces (meson fields) take over and shrink the radius still further. The large gravitational mass ratio of proton to electron thus forces nature to construct atoms from very small positive nuclei surrounded by extended electron clouds.

In addition to charge and mass, electrons and protons have a mechanical angular momentum, a spin; they behave like charged gyroscopes. A rotating charge is akin to a current circling an area; such a ring current produces a magnetic moment ($\mathbf{m}$) (Fig. 2). The ratio of this moment to the angular momentum ($\mathbf{p}'$) of the spinning particle is inversely proportional to the mass. Since the mechanical spin of the electron and proton prove to be identical ($\frac{1}{2}\hbar$, where $\hbar = 2\pi\hbar$ is Planck's constant), the magnetic moment of the electron, known as the Bohr magneton, is about 1836 times larger than the nuclear magneton of the proton.

By increasing the number of protons in the nucleus (the order number) in steps of 1 and simultaneously adding one electron each to the neutralizing negative atmosphere, the electrostatic sequence of the atoms of the periodic system results. [Actually, the formation of nuclei proceeds by complicated step reactions; hence, the abundance of elements gives a clue to the conditions prevailing at their creation (4).] Intuitively one is inclined to trace back the world, with its glorious variety, to the specific structure of the nucleus, which endows each atom type with a personality of its own. In fact, if we could see with x-ray eyes, the molecular world would appear as an eerie web of electron clouds anchored to positively charged points. These points, examined under much higher magnification, would resolve into spherical potential wells containing, deeply retracted because of their large mass, the nuclei. The actual composition, electric shape, and magnetic moment of these nuclei have only a minor "hyperfine-structure" influence on the electron clouds. The mutual constellation of the nuclear dots in space and the number of positive charges in each dot determine the texture and color of the electron fabric.

Thus, when we understand the electron structure of the atoms and their modes of interaction, we can weave and tear, mend and dye this fabric and thus design materials and devices.

Atom Structure

The hydrogen atom—proton and one electron—presents a two-body problem; its possible electron-cloud structures (orbitals) can be calculated accurately, while those of all other atoms—as multibody problems—can only be found by approximation. Thus, the results of the hydrogen atom have served, rightly or wrongly, as the prototype pattern for all atoms and must be briefly recalled (5).

There is a sequence of stationary energy states, characterized in their average distance from the nucleus by a principal quantum number n ; its integers $n = 1, 2, 3, 4, 5, \dots$ can be visualized as designating circular Bohr orbits, in circumference corresponding to $1, 2, 3, 4, 5, \dots$ electron wavelengths. The ground state $n = 1$ represents the deepest trap in which the proton can bind the electron (13.53 electron volts);

all other modes are a succession of excited states. This sequence of extending orbitals produces the shell structure of the atoms (see Fig. 1).

The ground state of the hydrogen atom binds the electron in a spherical probability pattern (s state); no direction of rotation is preferred, hence the electron has no orbital angular momentum in reference to the nucleus. For the excited states ($n > 1$), an increasing number of eccentric electron-cloud figurations ($l = n - 1$) are also stable solutions of the wave equation; these are characterized by orbital angular momenta $p' = [l(l+1)]^{\frac{1}{2}}$. The azimuthal quantum number $l = 0, 1, 2, 3, 4, \dots$ designates them as $s, p, d, f, g, \dots$ states, and the integer set (n, l) of two quantum numbers prescribes unambiguously the orbital type (standing-wave mode type) in which the electron finds itself.

It becomes apparent, when placing the hydrogen atom in a magnetic field, that each of these orbital types consists of $(2l+1)$ individual orbitals. The orbital angular momentum makes the atom a gyroscope and simultaneously creates an orbital magnetic moment (see Fig. 2). The external field exercises a torque on the gyroscope by coupling to this magnetic moment; the result is a precession around the field axis. Any recurrent motion in the molecular world characterizes a standing-wave mode; the transition from mode to mode requires a discontinuous, quantized energy step. Hence, the orbital angular momentum must assume discrete, quantized orientations with respect to the field axis; its projection on the field axis is $p'_z = m\hbar$, with the magnetic quantum number m ranging from l to $-l$. Thus, each orbital can be designated uniquely by a set of three quantum numbers (n, l , and m).

Finally, an electron placed into an orbital can orient its own angular momentum, its spin component $s\hbar$, either parallel or antiparallel to the field ($s = \pm \frac{1}{2}$); an electron in its orbital is therefore characterized by a set of four quantum numbers (n, l, m, s). Pauli's exclusion principle requires that particles with half-integer spins, like the electron, must be distinguishable each by its own set of four quantum numbers; that is, such particles obey Fermi-Dirac statistics. Each atomic orbital can thus only accept two electrons paired with antiparallel spins.

The periodic system, as presented in

VIII b															
2															
He															
IIIb IVb Vb VIb VIIb VIIIb															
5 6 7 8 9 10															
B C N O F Ne															
13 14 15 16 17 18															
Al Si P S Cl A															
31 32 33 34 35 36															
Ga Ge As Se Br Kr															
49 50 51 52 53 54															
In Sn Sb Te I Xe															
81 82 83 84 85 86															
Tl Pb Bi Po At Rn															
Ia IIa IIIa IVa Va VIa VIIa VIIIa Ib IIb															
21 22 23 24 25 26 27 28 29 30															
Sc Ti V Cr Mn Fe Co Ni Cu Zn															
39 40 41 42 43 44 45 46 47 48															
Y Zr Nb Mo Tc Ru Rh Pd Ag Cd															
57 72 73 74 75 76 77 78 79 80															
La Hf Ta W Re Os Ir Pt Au Hg															
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57 58 59 60 61 62 63 64 65 66 67 68 69 70 71															
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu															
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89 90 91 92 93 94 95 96 97 98 99 100 101 102 103															
Ac Th Pa U Np Am Pu Cm Bk Cf Es Fm Md No Lw															
f															

Fig. 3. Periodic system based on hydrogenlike orbitals.

Fig. 3, assumes that the multi-electron systems of the atoms can be described by hydrogen-like orbitals. We have the various shells (n) and subshells (l) of orbital type $s, p, d, f, g, \dots$. Since an orbital can accommodate two electrons and each orbital type has $2l + 1$ orbitals, the subshells are filled when they contain $2(2l + 1)$ or 2, 6, 10, 14, 18, $\dots$ electrons, respectively. The electron distribution of an atom can be written in shorthand by giving the integer number of the shell and the letter of the subshell, with the number of occupying electrons as superscript; for example, the electron distribution in the Fe atom (order number 26) is represented unambiguously by the symbol $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$.

Here appears our first predicament: only experiment can make it clear that subshell $3d$ takes in six electrons, leaving two in the $4s$ orbitals. The sudden filling of inner d and f subshells shown in Fig. 3 certifies that the mutual energy relations between shells and subshells change with occupation. Furthermore, we can foresee that the energy states, especially those of the outer shells, will be altered by interaction with the surroundings.

Nature designs everything from atoms; hence, we should be able to design any kind of material with foresight if we thoroughly understood the periodic system in all its implications. At this stage—like weather forecasters—we are still members of the gambling profession.

Elements and Compounds

Atoms are not the inert building stones of fixed size, shape, and connecting links that a model designer has to pretend they are. Isolated, they appear spherical and may be described by some nearest-approach distance: an atomic radius (when neutral) or positive and negative ionic radii (when they shed or trap electrons). However, the distortion of electron clouds by approaching neighbors creates polarity, ranging all the way from a weak van der Waals attraction by fluctuating dipole moments—caused by phase relations between electrons of interacting clouds that try to avoid each other—to the strong permanent dipole moments of polar molecules. Furthermore, atoms are inherently endowed by their eccentric electron clouds with strong

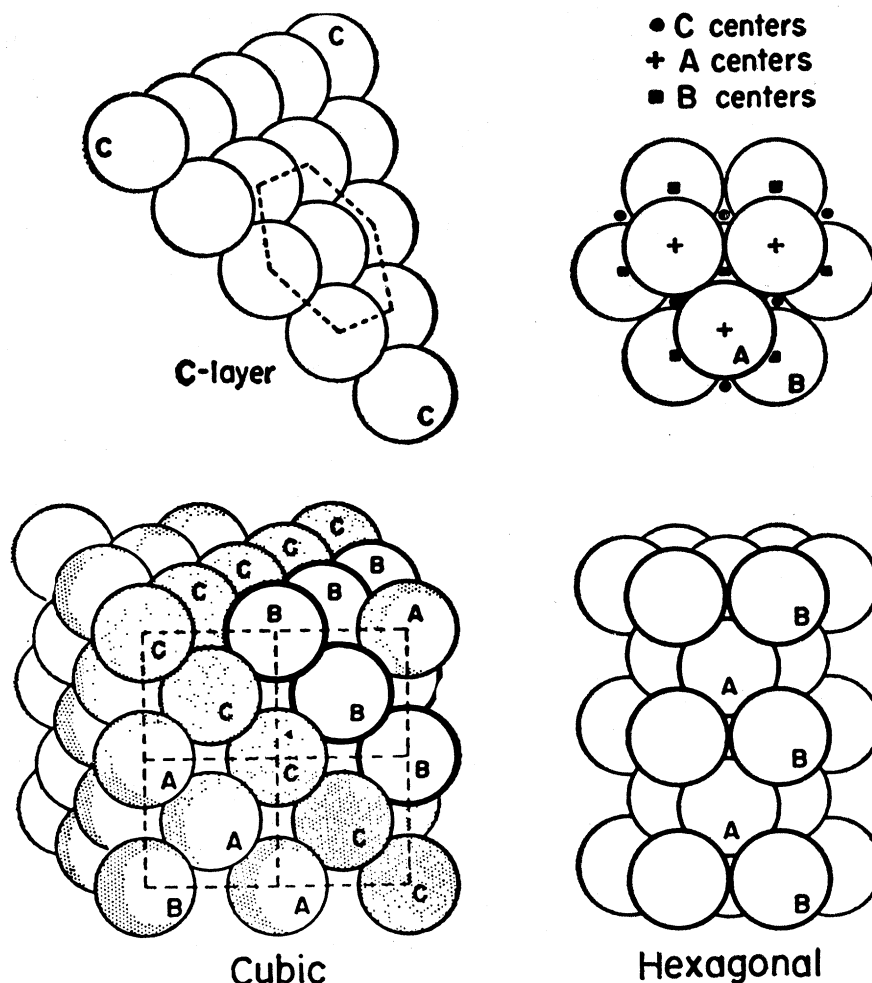


Fig. 4. Close-packed arrays of spheres.

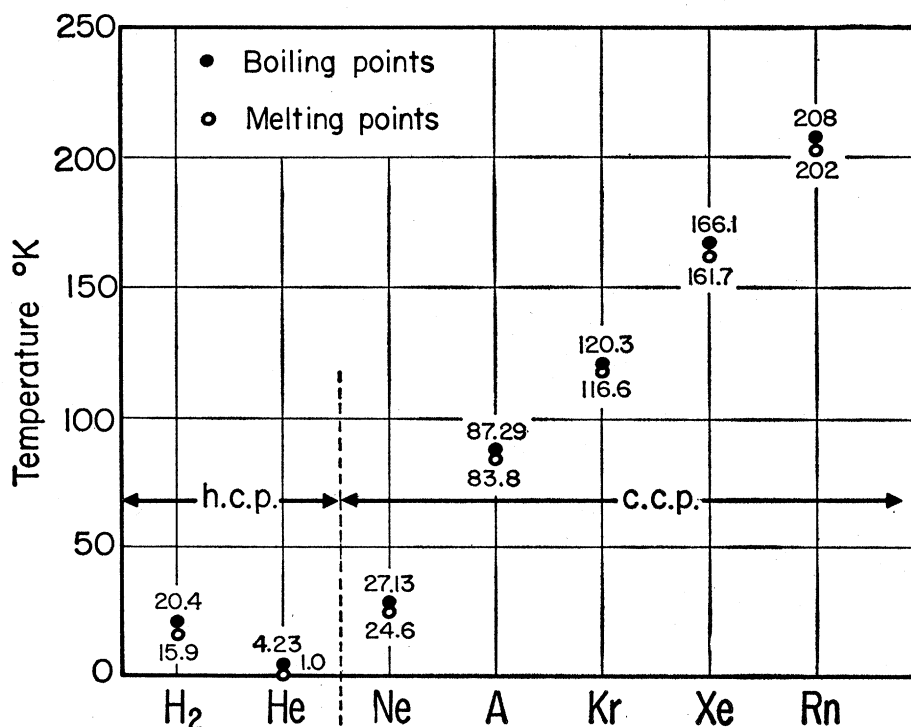


Fig. 5. Melting and boiling points of H₂ and the rare gases.

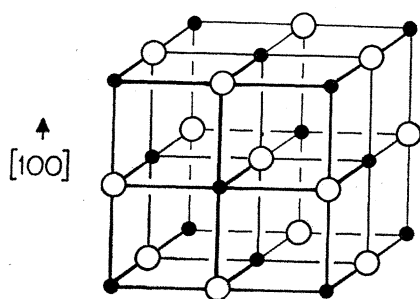
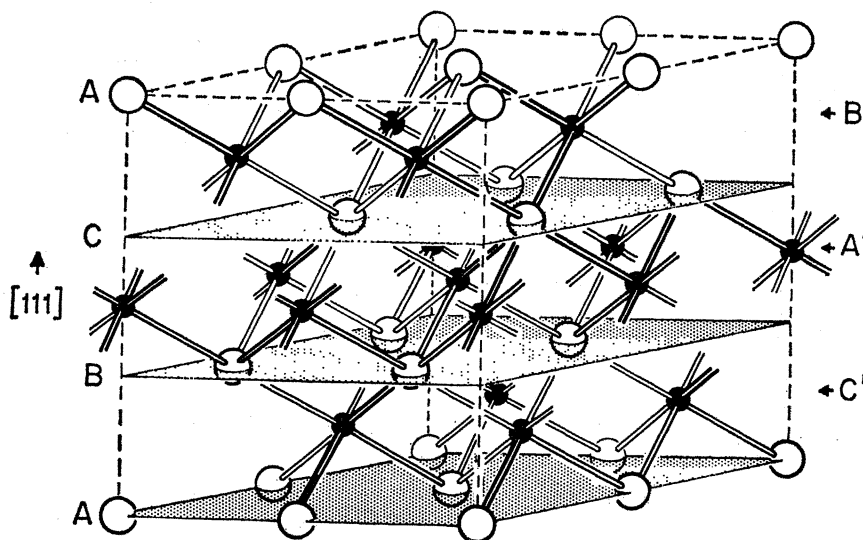


Fig. 6. Rock salt structure as related to close-packed structure.



stereoproperties. Hence, the valence electrons of unfilled outer shells form strong directive links (ligands) with their neighbors.

Gilbert N. Lewis first recognized the electron-pair bond which allows the $1s^1$ electrons of two hydrogen atoms to pair in antiparallel spin orientation, forming molecular hydrogen, H_2 , or which allows alkali halide molecules to acquire the octet structure s^2p^6 of rare-gas atoms. Obviously, the originally spherical electron distribution has been drastically altered by such diatomic molecule formation, to the cylindrical symmetry of dinuclear systems. The overlap of the previously isolated electron clouds becomes a measure of the bond strength. The valence electrons have been saturated, nearly equally strong diatomic molecules H_2 or $NaCl$ have been formed (about 103 and 97 kcal/mole, respectively), and one might expect that such molecules will be inert, like rare-gas atoms.

Rare gases cannot form directed bonds as long as their saturated spherical electron-cloud system remains unbroken by excitation. Hence, only the weak van der Waals attraction acts, packing the atoms as equal spheres, like oranges in crates, in one of two densely packed arrays (Fig. 4): in planes with repeat sequence $ABAB \dots$ or $ABCABC \dots$, yielding hexagonal or face-centered cubic crystals, respectively. In both cases each atom is surrounded by 12 neighbors at equal distances (coordination number $CN = 12$). Very low melting and boiling points result, indicating with their rising trend from helium to radon that the cohesion increases with the number of participating electrons (Fig. 5).

The hydrogen molecules act according to expectation: they pack as densely as possible by van der Waals forces without losing their identity; melting and boiling points are low. The individual alkali halide molecules, in con-

trast, by condensing lose their identity; they are dissolved, with large energy release, in the ionic rock salt structure. Still, there is a memory left of the rare-gas behavior when this structure is properly drawn: Na^+ and Cl^- separately have rare-gas shells and form two interleaving sublattices of the cubic close-packed type (Fig. 6).

Turning to the second row of the periodic system we may predict that lithium and boron, with a lone $2s^1$ and $2p^1$ electron, respectively, will form Li_2 and B_2 molecules in analogy to H_2 , and that beryllium, with its $2s^2$ electron pair, will remain monatomic like a rare-gas atom. This is almost true, but instead of condensing into insulating liquids at low temperature, lithium and beryllium become metals and boron becomes a semiconductor. Melting and boiling points (Fig. 7) rise high, and only from nitrogen on is the rare-gas behavior resumed by diatomic molecules (as in the case of H_2).

That alkali atoms form metals might have been surmised by their tendency in the alkali halides to regain their rare-gas shell by shedding the lone electron. Thus, the fixed anion sublattice in Fig. 6 can be visualized as being replaced by a mobile electron lattice. The fact that the alkaline-earth atoms share their two electrons in metallic bonding is an extension of this situation. However, the structure of the boron crystal is a complete surprise: its tetragonal unit cell contains four icosahedra of 12 atoms each with ligancy 6 and two interstitial boron atoms of ligancy 4 that knit these regular polyhedra together (Fig. 8) (6). Thus, the boron atom with its three valence electrons can contribute only a fractional electron charge to its six or four bonds, respectively.

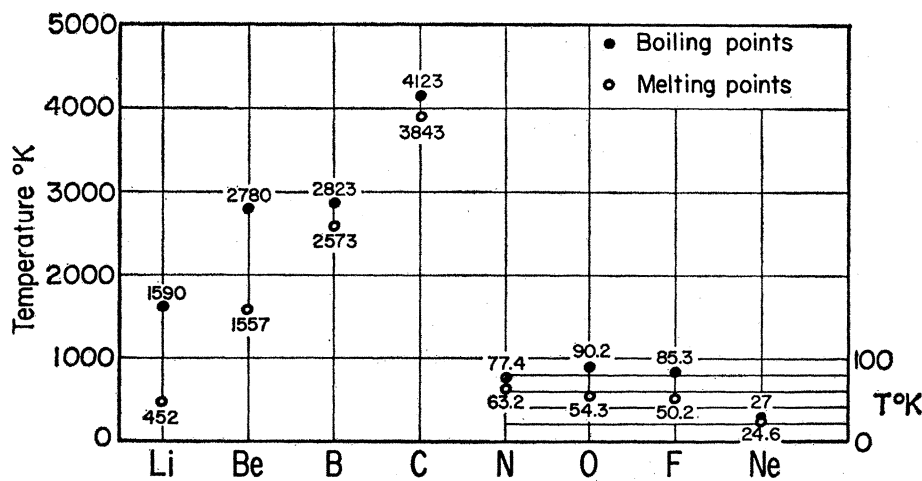
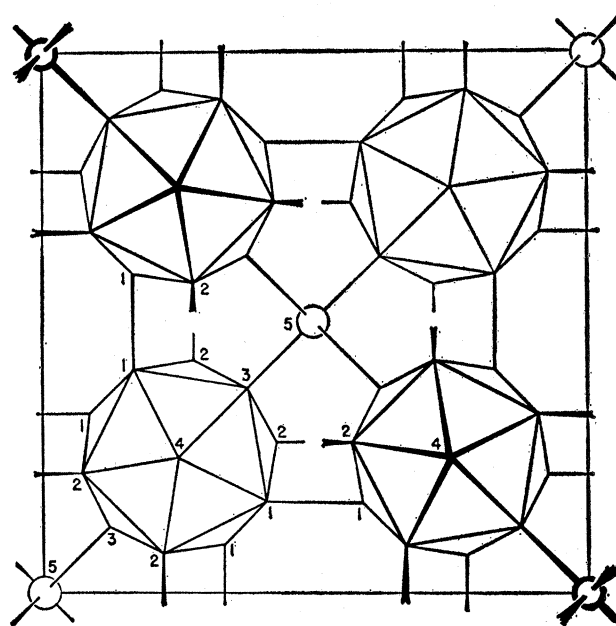
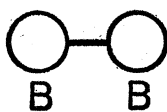
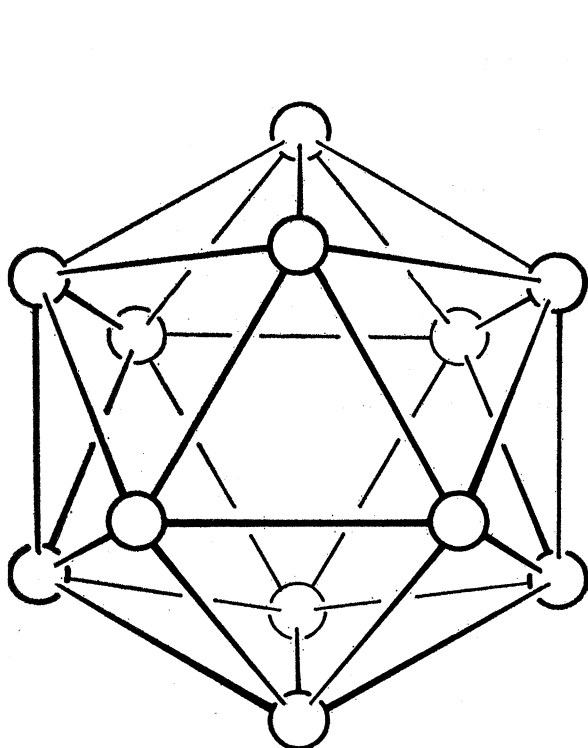


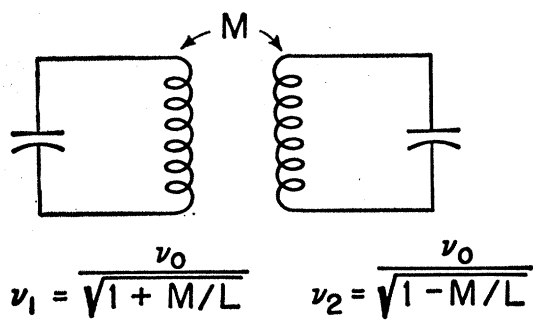
Fig. 7. Melting and boiling points for the elements of the second row.



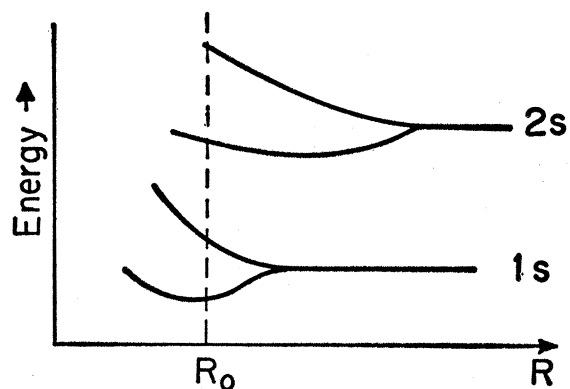
An icosahedral B_{12} group

Projection

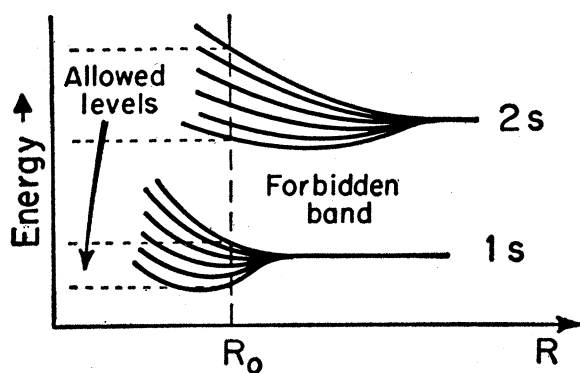
Fig. 8. The structure of boron. [After Pauling (6)]



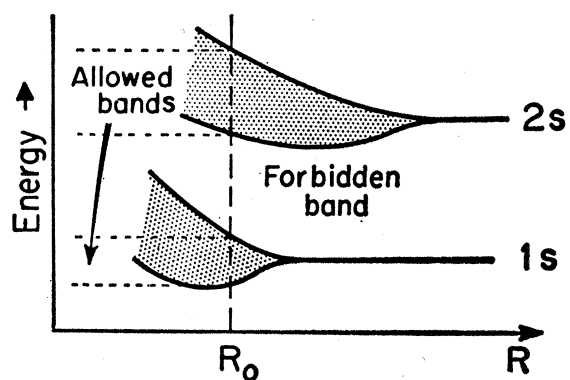
Classical analog



Two atoms



Six atom linear chain



n -atom crystal

Fig. 9. Coupling of classical oscillators and band structure of crystals.

Obviously, the concept of clamping atoms together with their hydrogen-like $s, p, d, \dots$ orbitals in pair-bond formation, thereby saturating valencies, and then packing tightly does not suffice. We have neglected the fact that the electron-density patterns assigned to each standing-wave mode actually spread over all space. Hence, coupling must occur between all mutually compatible electron modes inside atoms as well as between neighbors. Such coupling is well known in the case of classical oscillators and splits a resonant mode into a higher and a lower frequency band (Fig. 9). Similarly, the

individual energy states of atoms split (i) within the atoms themselves, by magnetic coupling of orbital and spin moments (internal Zeeman effects) and by electrostatic interaction (internal Stark effects), and (ii) through external interactions with neighboring atoms, again by coupling of orbital and spin momenta and by reacting to electrostatic effects (for example, the crystal fields of solids).

One simple outcome of this splitting of energy states is the well-known Bloch-Wilson model classifying crystals as insulators, semiconductors, or metals according to the separation or overlap

of the energy bands in which electrons or holes may transfer through a periodic lattice structure. Much ingenious work is at present devoted to the elucidation of the actual stereostructure of such bands, as seen from the standpoint of electrons and their wavelengths (that is, in k space) (7).

A second result of the coupling of wave modes is that combinations of such modes can be excited like the timbre of a musical instrument. In simple cases only two wave-function types may dominantly be involved, as in the celebrated s - p hybridization of the carbon atom, which starts organic chem-

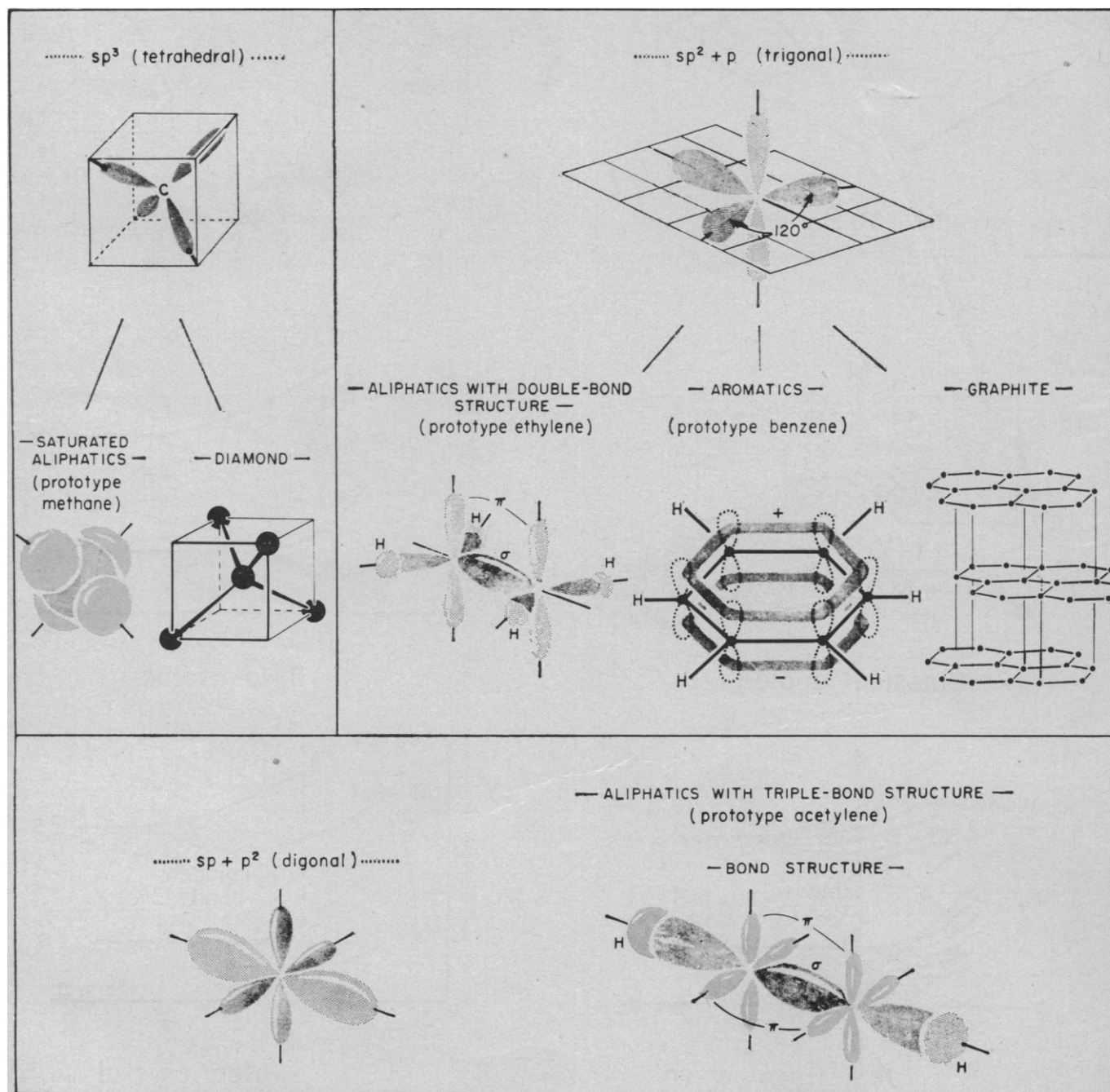


Fig. 10. Hybrid bonds of carbon.

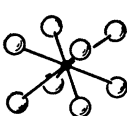
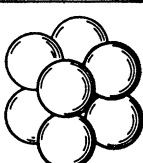
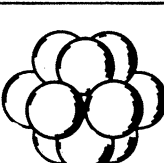
r_c/r_a	CN	Type of site	
0.155 ↔ 0.255	3	 Triangular	
0.255 ↔ 0.414	4	 Tetrahedral	
0.414 ↔ 0.732	6	 Octahedral	
0.732 ↔ 1.00	8	 Cubic	
1.00	12	 Densest packed	

Fig. 11. Radius ratio and coordination.

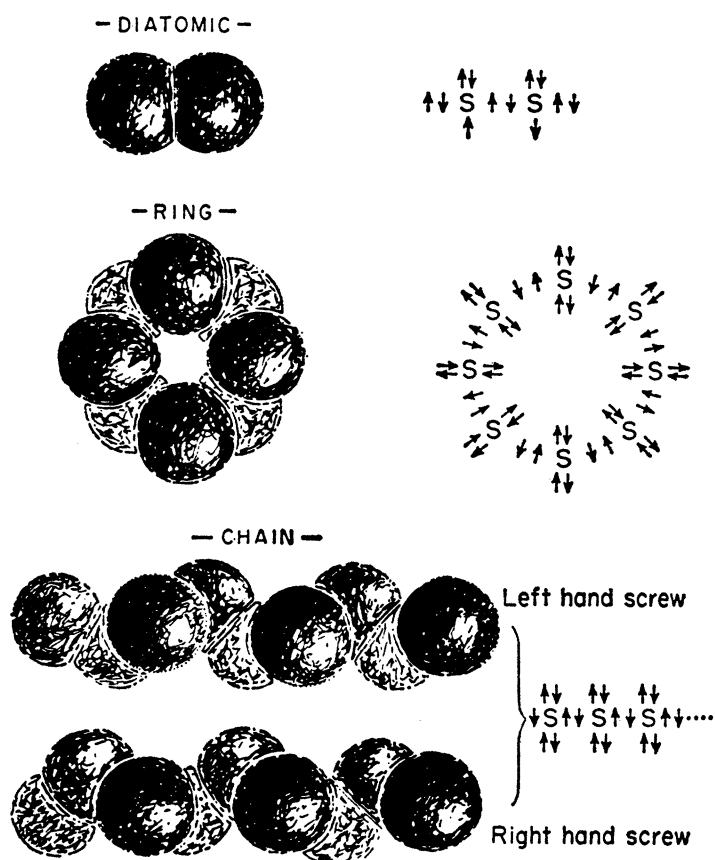


Fig. 12. Various types of sulfur molecules.

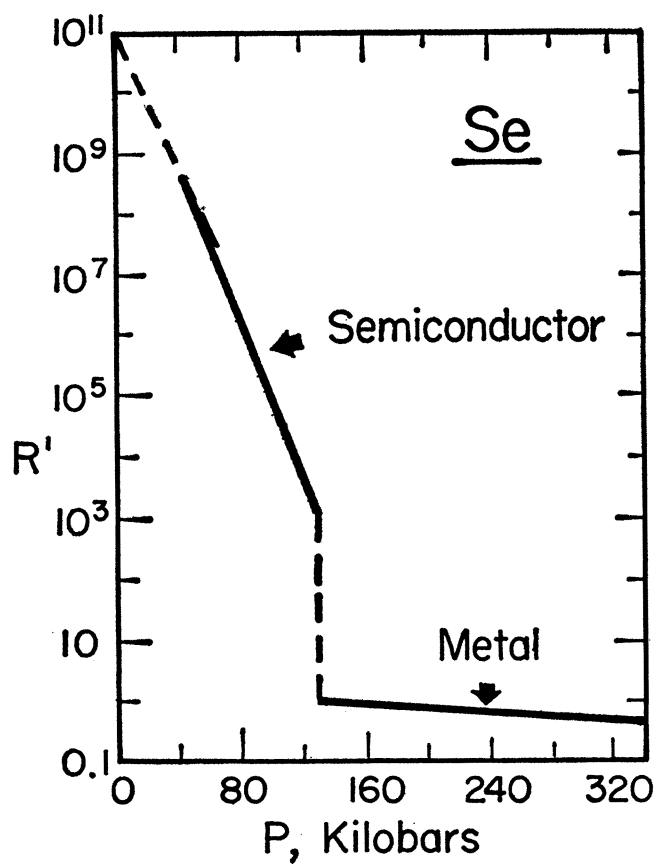
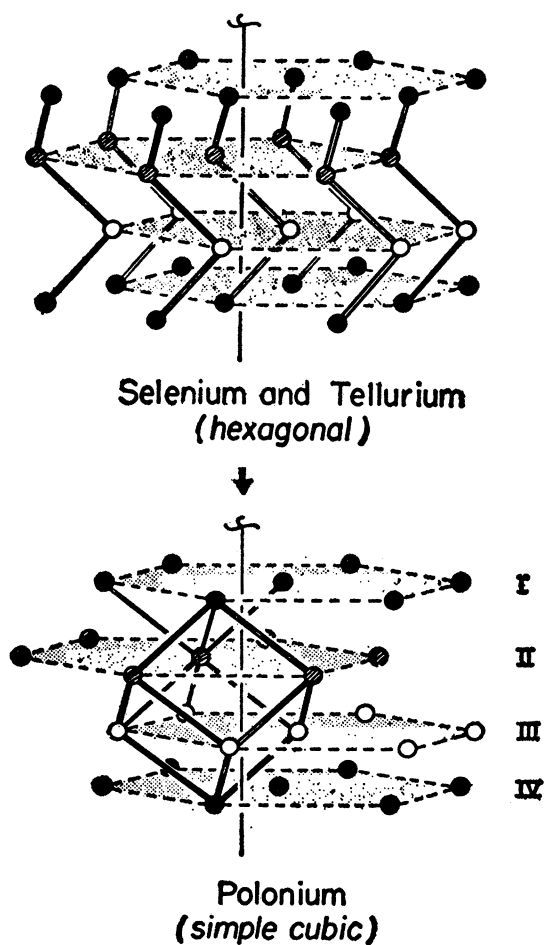


Fig. 13. Selenium- to polonium-type transition. [After Balchan and Drickamer (9)]

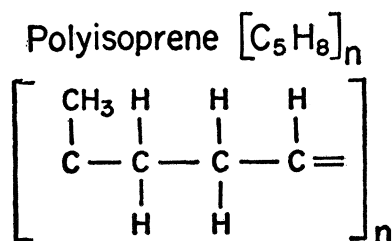


Fig. 14 (above and right). Stereoisomerism of polyisoprene.

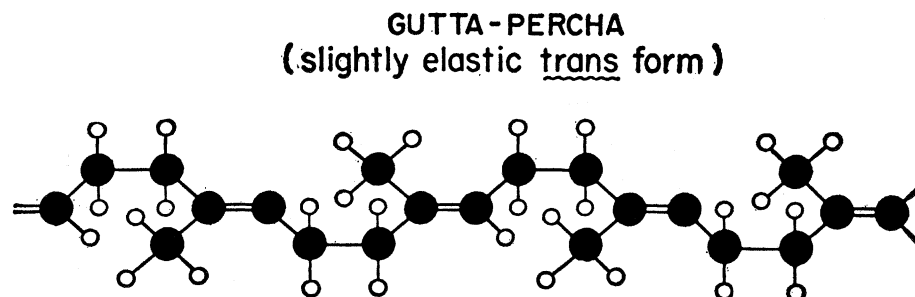
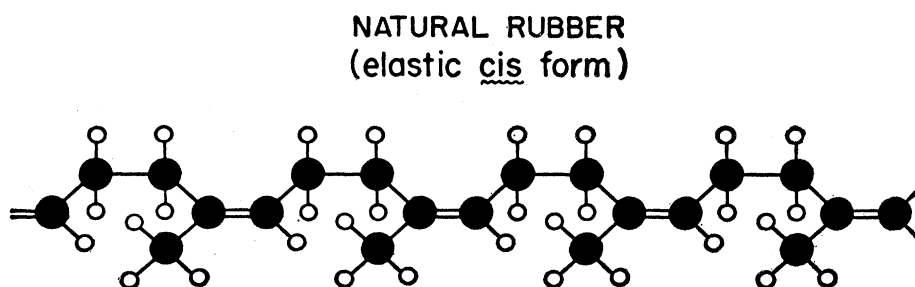
istry on its way with aliphatic and aromatic compounds (Fig. 10). Here pair-bonds still suffice, but the structure of boron (see Fig. 8) makes it obvious that individual electrons may spread themselves over various compatible wave modes. Thus, the actual structure can be visualized as containing genes of a variety of individual constellations, each making its contribution to the structure, properties, and cohesive strength of the final array. This is the concept of quantum-mechanical resonance, used so successfully by Pauling (6) in describing the nature of the chemical bond.

Molecules and Crystals

Such latent properties of electron-cloud formation, called to the fore as the environment dictates, makes designing with atoms an occupation filled with curious anticipation, like gardening in a greenhouse: select the seeds, set the conditions of the surroundings, and things begin to happen.

Three extreme cases became apparent in the preceding discussion:

1) Atoms may stay single in the



gaseous phase because they are inert (rare gases), or they may form semi-inert molecules by saturation of primary valence bonds (for example, H_2). Weak secondary attraction condenses these entities into close-packed phases without destroying their identity; low melting and boiling points result (see Figs. 5 and 7).

2) Atoms stay single in the gaseous phase (for example, beryllium) because strong primary bonds develop only in multiatomic clusters where common wave functions can bind the array; an electron community arises, usually leading to the metallic state. This is a very common situation, since three quarters of all elements are metals; higher melting or boiling points, or both, and monatomic vapors are the rule.

3) Molecules form in the gaseous state by valence bonding but are torn to pieces by stronger primary bonds of the condensed phases. The cause may be the polarity of the molecule, leading to the far-ranging Coulomb fields of an ionic lattice structure (for example, sodium chloride) (see Fig. 6). It may be the community of metal electrons that dissolves the molecule, as in the case of Li_2 , or covalent links between nearest neighbors may in continuous sequence build strong three-dimensional networks, as in diamond; two-dimensional planes, as in graphite; or linear chains stretching through space, as in carbon polymers (see Fig. 10).

In their extreme form, metallic and ionic bonds act according to the principle *horror vacui*, compacting and tending to fill space as densely as the radius

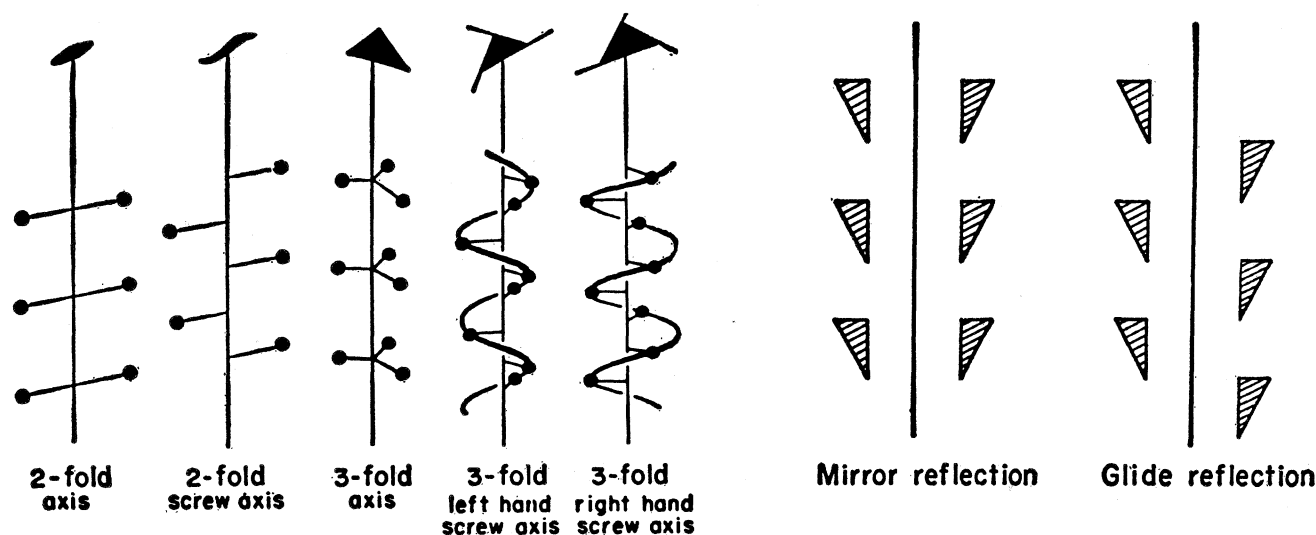


Fig. 15. Various types of symmetry elements.

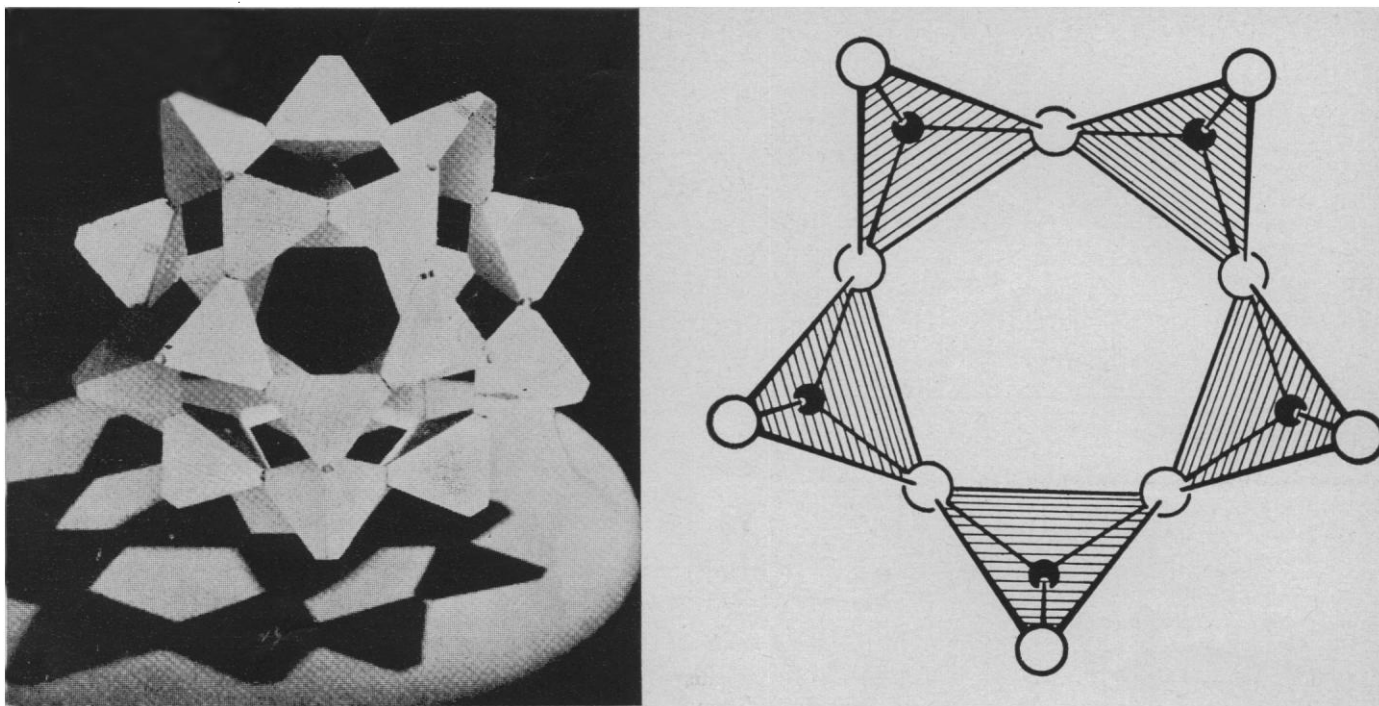


Fig. 16. Pentagonal dodecahedral groups in silicate glass or water. [After Tilton (12)]

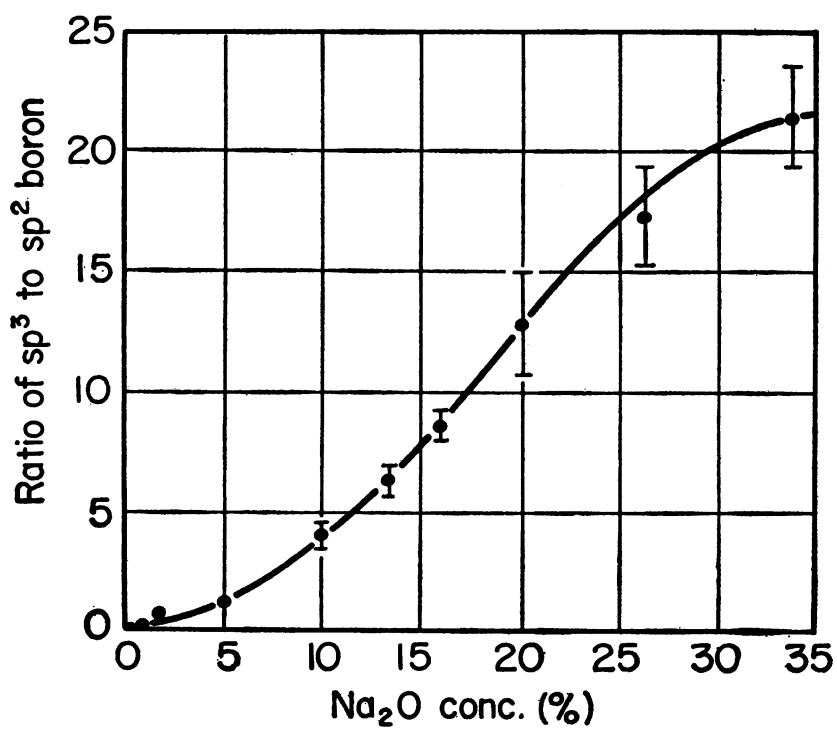
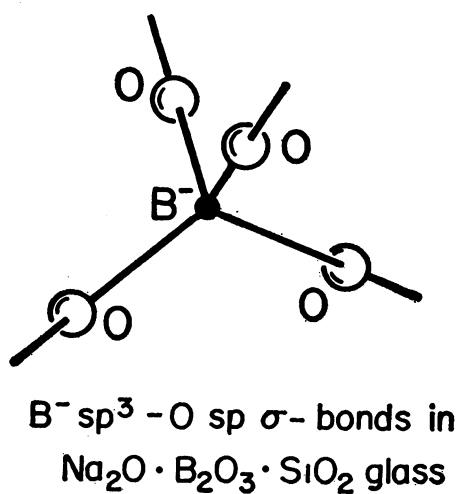
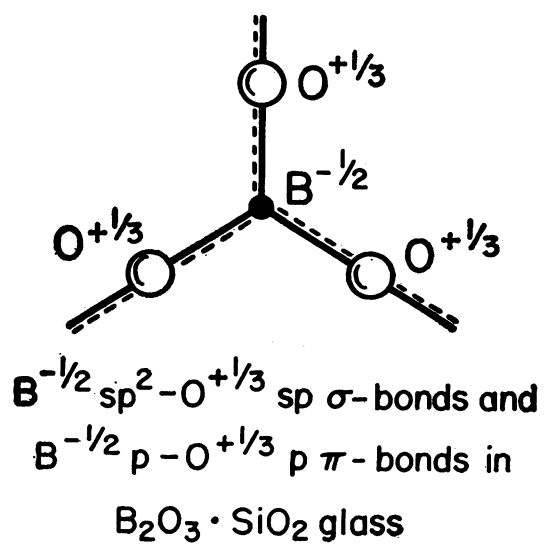


Fig. 17. Competing coordinations of B^* in sodium borosilicates. [After Silver and Bray (14)]

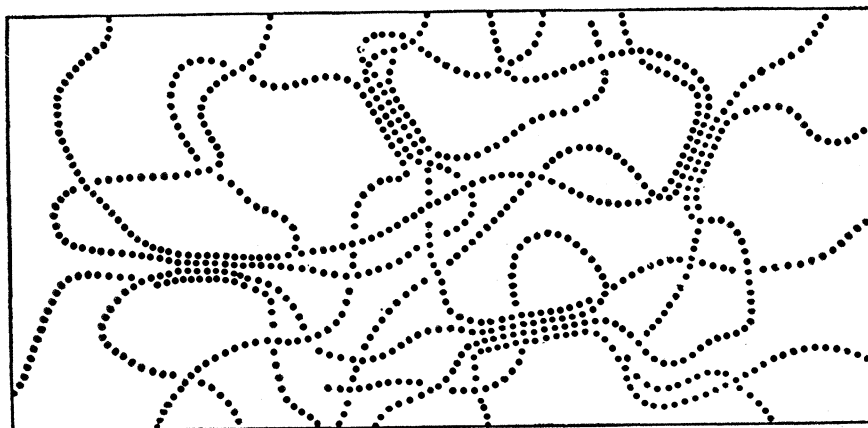
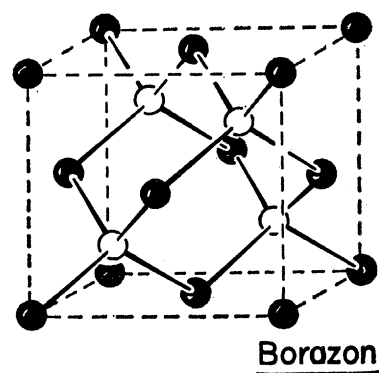
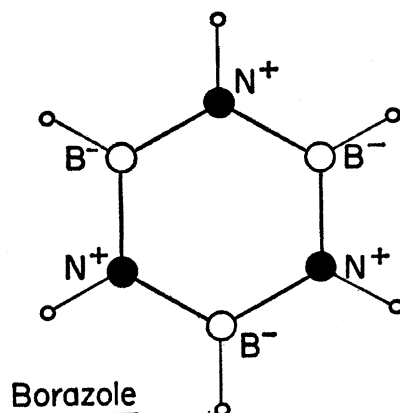
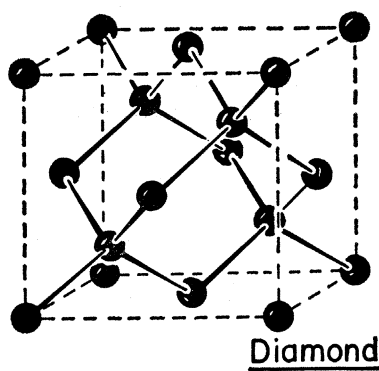
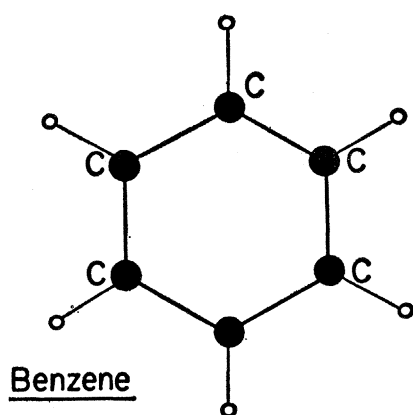
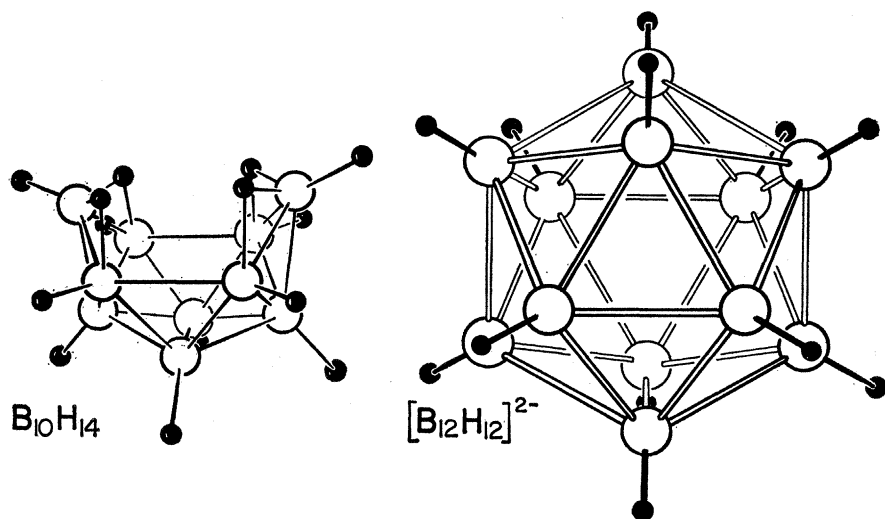


Fig. 18 (top). Combination of amorphous and crystalline regions.

Fig. 19 (middle). Polyhedral molecules of boron hydrides.

Fig. 20 (bottom). Structure preservation by averaging nuclear charges.



ratio of the partners permits (Fig. 11). In contrast, the short-ranging, strongly directive covalent bonds are the primary tools of imaginative architecture. Actually, this distinction is blurred in nature, because any bond between unlike atoms imparts polarity; even shared electron clouds can move in cooperative polarity against the residual structure.

The diversity of nature stemming from the various bonding possibilities of more than a hundred atoms would be staggering even if the structure of a material were determined uniquely by temperature and chemical composition. Actually, as everyone knows when ordering his egg boiled, fried, or scrambled, there often are multiple choices in arranging the same elementary constituents. Prehistory enters for samples as for living beings, as a codeterminant of their present state.

In its simplest form, this prehistory dependence becomes apparent in the polymorphism of elements. Oxygen gas, for example, consists normally of $O=O$ molecules, because the double bond is stronger than two single bonds; sulfur and selenium vapor, on the other hand, tend to contain S_8 or Se_8 ring molecules, because two single bonds are stronger than one double bond (Fig. 12). The double bond, however, is still much stronger than a single bond; hence, the composition of the vapor phase changes with increasing temperature from eight-membered rings to diatomic molecules. When the ring molecules break open, the possibility of chain polymerization arises, as is well known from the formation of plastic sulfur. At room temperature this material reverts to the brittle ring structure, but selenium occurs in stable crystals built from rings or chains and also in amorphous chain-polymer modifications. In the ring form, selenium is an insulator; in the chain form, a semiconductor, since electron defects can be transferred along the chains. When squeezed by very high pressure—as might be expected from the structure relation to tellurium and the metal polonium (8)—selenium becomes a metal (Fig. 13) (9).

Since high temperature breaks down preexisting molecular entities and high

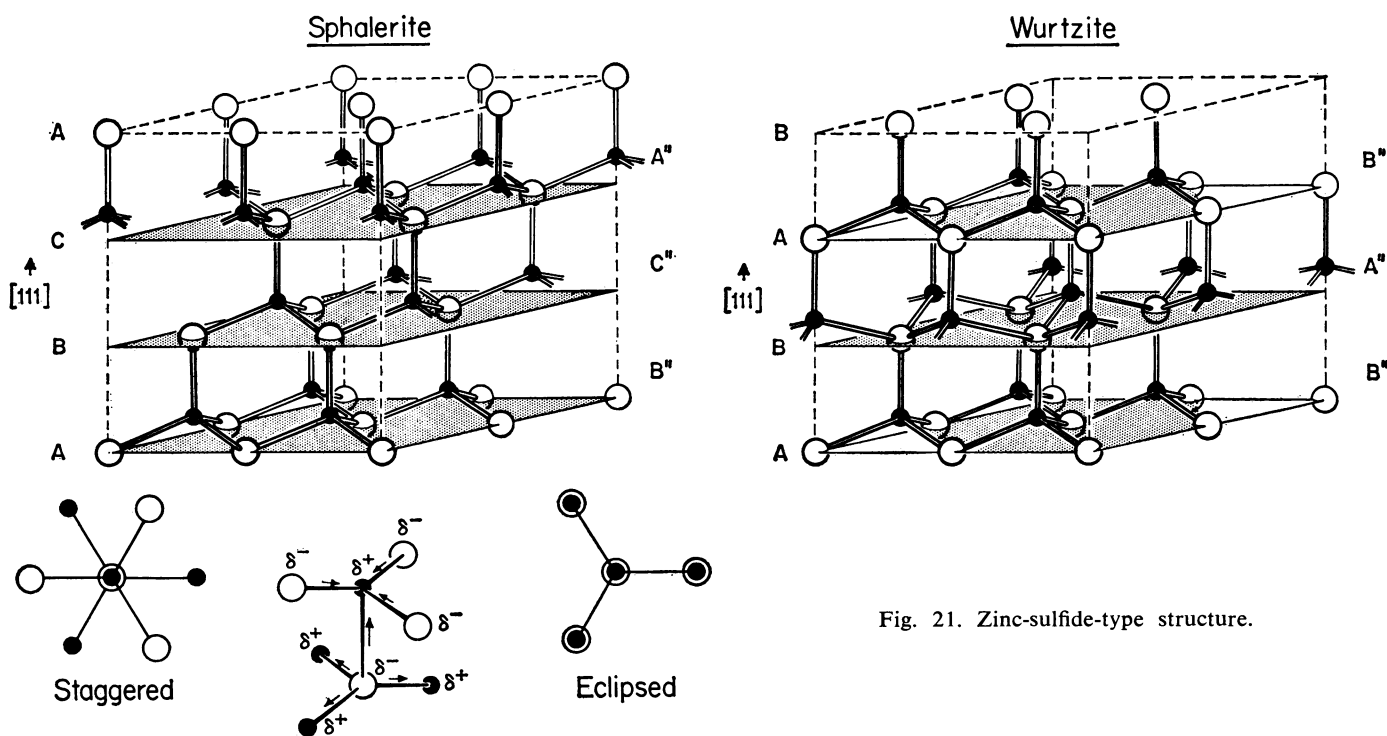


Fig. 21. Zinc-sulfide-type structure.

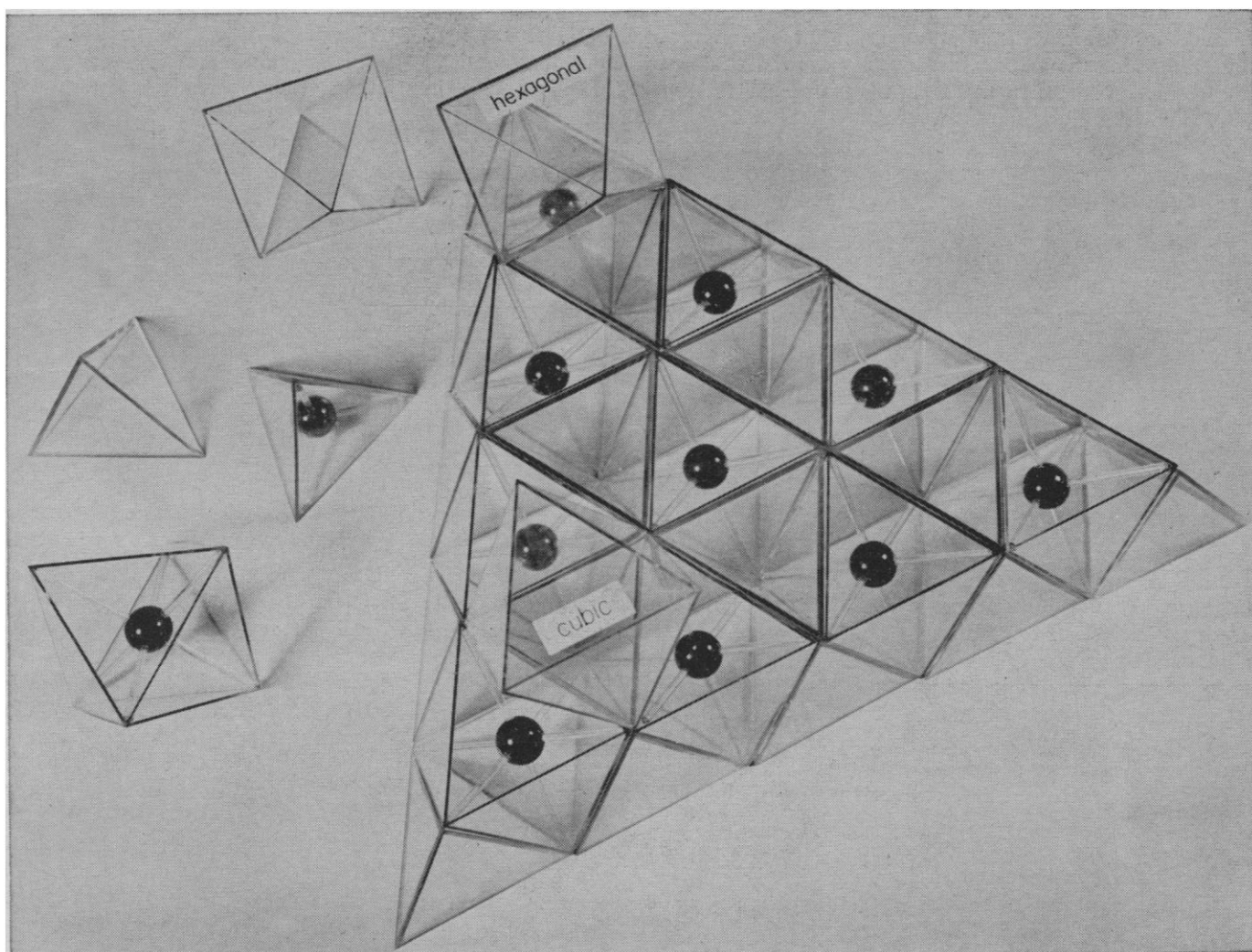


Fig. 22. Close-packed structures built from interstitial tetrahedra and octahedra.

pressure holds the constituents at effective interaction distance, high-pressure, high-temperature techniques are of increasing importance for synthesizing modifications normally precluded by interfering bond formations. The synthesis of diamond, of boron nitride in diamond instead of graphite structure, and of the new silicon dioxide modification coesite—which is proving so useful to the geologist in identifying craters of meteoric origin—are outstanding accomplishments of this approach (10). Synthesizing materials from defined elementary particles by molecular-beam techniques in ultrahigh vacuum is another promising method still in its pioneering stages.

Allotropy and the existence of competing structure types lead automatically to the subject of phase transitions. With falling temperature a material normally contracts, overlap and interaction time between electron clouds increase, and randomizing thermal agitation subsides. Thus, crystals at high temperature tend to be more symmetrical and more tolerant of substitutions, while in cooling the weaker, more specific interaction forces emerge from the sea of thermal noise and enforce special types of order, thereby lowering the crystal symmetry. If this reorganization is incompatible with the preexisting lattice and if the new arrangement can nucleate, the sample will shatter and recrystallize in a first-order transition. On the other hand, a completely continuous transformation may be possible, as is well known from the disorder $\rightleftharpoons$ order transitions of the constituents of alloys, the magnetic moments of electrons forming the spin systems of ferro- and antiferromagnetics, or the electric moments of polar crystals organizing in dipole chains of piezo- and ferroelectrics (5). The time taken by such phase transitions may range all the way from instantaneous explosion or thermal hysteresis of nanosecond duration to the millions of years traceable in geological strata.

Competing types of order are of decisive importance in the organic world. Whether polyisoprene assumes the *cis*- or the *trans*- structure decides whether a useful elastic rubber or an inelastic balata is obtained (Fig. 14). The ordering of water molecules twists protein molecules into spiral structures decisive for life processes (11), and here again the differentiation into right-hand or left-hand screw structures is vital for the activation of such processes.

Laws of Molecular Architecture

A great variety of individual design concepts have appeared in the preceding discussion: hydrogen-like wave functions of atoms and electron-pair bonding; modifications of simple atomic orbitals by hybridization; combinations described by quantum-mechanical resonance; splitting of energy states by coupling, leading to molecular orbitals and the band structure of crystals; dense packing, as far as radii and their ratio allow; molecular, ionic, covalent, and metallic structures; polarity, polymorphism, and isomers; phase transitions and the importance of prehistory. With the development of magnetic-resonance techniques and devices such as masers and lasers, more and more becomes known about the fine structure of energy states, and the introduction of increasingly powerful computers makes it possible to calculate wave functions with rapidly increasing reliability. We learn—but a nightmarish feeling begins to assail the scientist, of becoming lost in the labyrinth of the Minotaur. Where are the guiding principles that can lead through this maze of phenomena in graphic understanding?

At the outset we stated that the space correlation and charge of the nuclei are the primary determinants for the web of electron clouds; hence, topology should be a guide. Judged from this point of view the structures of molecules and crystals are characterized by the presence (or absence) of certain elements of symmetry: a center of symmetry, planes of reflection or glide reflection, and axes of rotation and screw rotation (Fig. 15). For crystals the stringent requirement of periodic repetition of lattice points limits the admissible periodicity in rotation to 1-, 2-, 3-, 4-, and 6-fold axes and the possible number of space groups to 230. Structure analysis can assign any crystal to one of these 230 compartments.

This type of classification, based on inherent properties of symmetry, is more exact than the Linnaean system, which orders the world of plants, but no more informative. We seek elucidation of the type provided by Darwin's *Origin of Species*: What kinds of structures are chosen for molecular reasons? Which rules guide their design and assure stability—that is, "survival of the fittest"?

Answers to these questions begin to evolve, but they will often not be unique, because a variety of molecular

causes can hide behind the same macroscopic phenomenon. For example, violation of the rule, just stated, that the long-range periodic order of crystalline networks permits only 1-, 2-, 3-, 4-, and 6-fold axes of rotation should allow the forcing of materials into the glassy state of short-range order. This was suggested years ago by Tilton (12), who, in building models of silicates, demonstrated the likely occurrence of groups with 5-fold axes; and a very similar kind of arrangement has been invoked by Pauling for explaining the hydrogen-bonded structure of water (Fig. 16). On the other hand, the symmetry of molecular groups need not transfer to a crystal structure, as is demonstrated by boron, whose icosahedra of 5-fold rotation symmetry are safely tucked away in a unit cell of tetragonal symmetry (see Fig. 8), or by virus particles with 5-fold axes assembled in a close-packed crystal structure.

There are other causes of glass formation: the competition of various molecular constellations on the basis of nearly equal probability—as, for example, in borosilicates, where B^{3+} can enter in either triangular or tetrahedral bonding, as demonstrated by Warren and Bray (Fig. 17) (13, 14); the agglomeration of chain molecules to form glassy polymer structures; or the freezing-in of amorphous structures through suppression of nucleation. By developing crystal nuclei afterwards in glass systems, Stookey (15) pioneered the new pyroceramics, materials that combine the strength of crystalline with the bounce of amorphous regions (Fig. 18)—a trick used by nature in the growing of trees and the formation of muscle fibers.

To return once more to molecular design, the recent spurt in the recognition of polyhedra molecules has made it clear that practically any structure which seems topologically reasonable can be made, and that increased symmetry, *ceteris paribus*, imparts increased stability. A good example is the sequence of boron hydride molecules studied by Lipscomb and his co-workers (16). The regular icosahedral molecule $[B_{12}H_{12}]^-$ (Fig. 19) proved so stable that it could be injected into a patient in large doses for cancer treatment by neutron bombardment, while the semi-finished $B_{10}H_{14}$ structure would have been broken down in the body of the victim, causing his speedy demise.

The designing of materials could

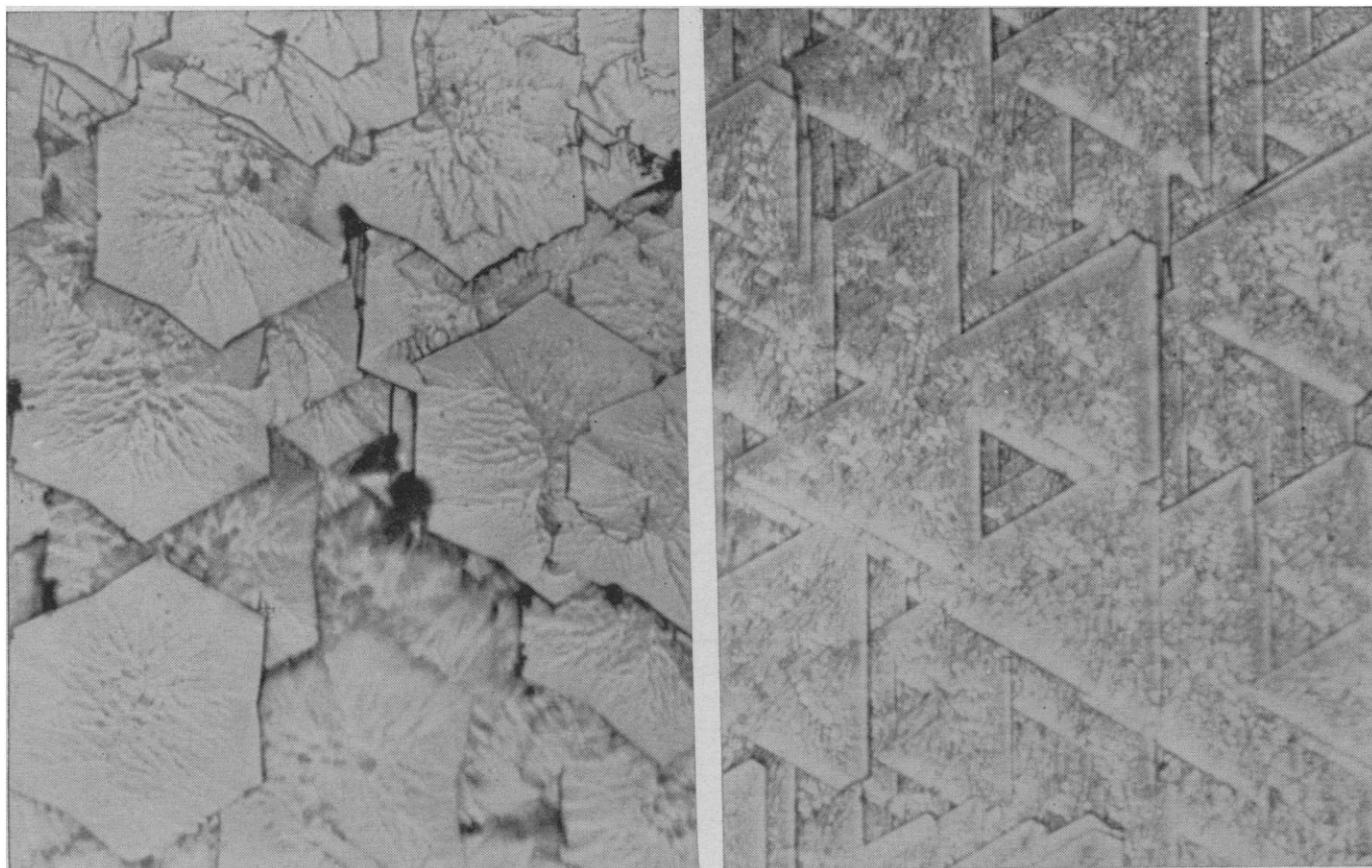


Fig. 23. [111] surfaces of indium antimonide etched for 30 minutes at 80°C (0.2N Fe^{3+} in 6N hydrogen chloride): (left) indium surface; (right) antimony surface (about $\times 495$). [After Gatos (18)]

start with molecular topology: tentative selection of the space arrangement of nuclei would prescribe the symmetry conditions—formulated by group theory—to which the system of interlinking electron clouds is subjected. Recourse to two types of restrictions, “tolerance conditions” and “property conditions,” would then lead systematically to alterations in the proposed array and to specific choices in the selection of nuclei. The procedure is akin to that of an architect who sketchily outlines a building and then, by carefully considering the restrictions imposed by the requirements of mechanical stability and function of the structure, arrives at choices of final design.

Tolerance conditions for a proposed structure are of molecular origin and specify the limits within which alterations in charge distribution and distortions of the space arrangement can be made without causing instability. Property conditions, by contrast, originate as macroscopic specifications for the performance of a material or device and have to be translated into molecular prescriptions.

Figure 20 illustrates the action of

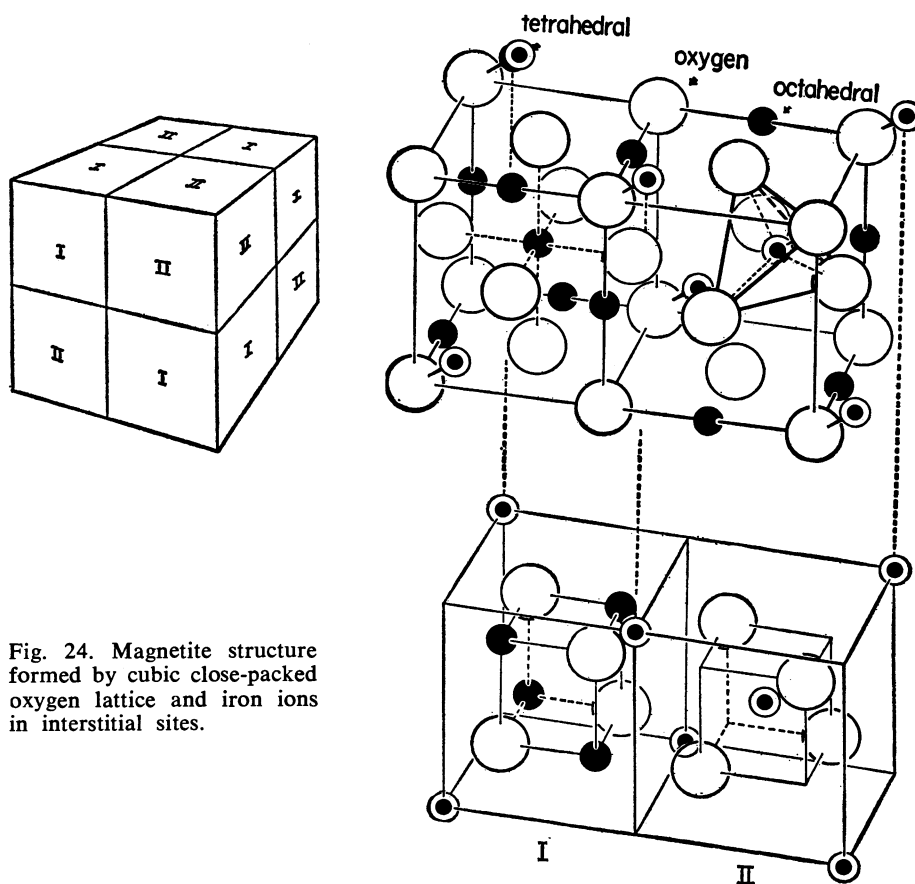


Fig. 24. Magnetite structure formed by cubic close-packed oxygen lattice and iron ions in interstitial sites.

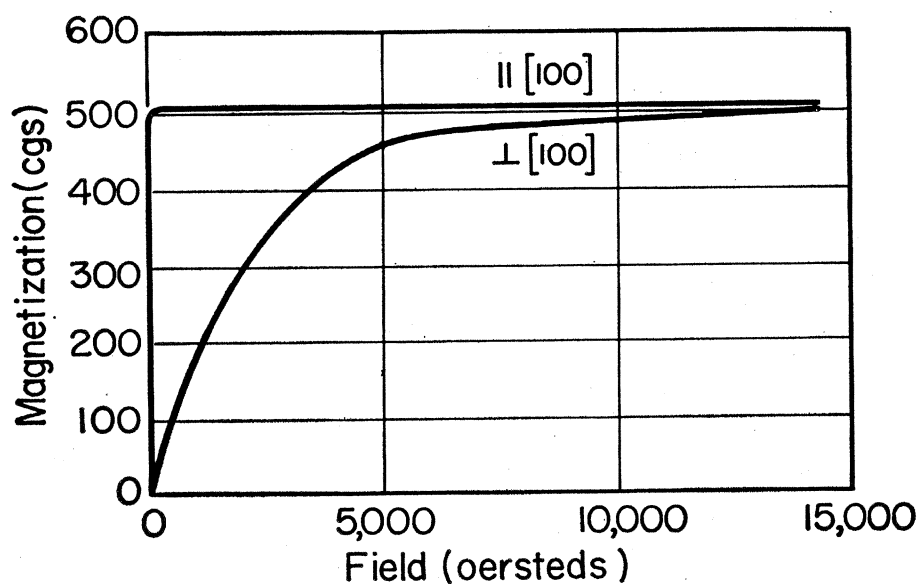
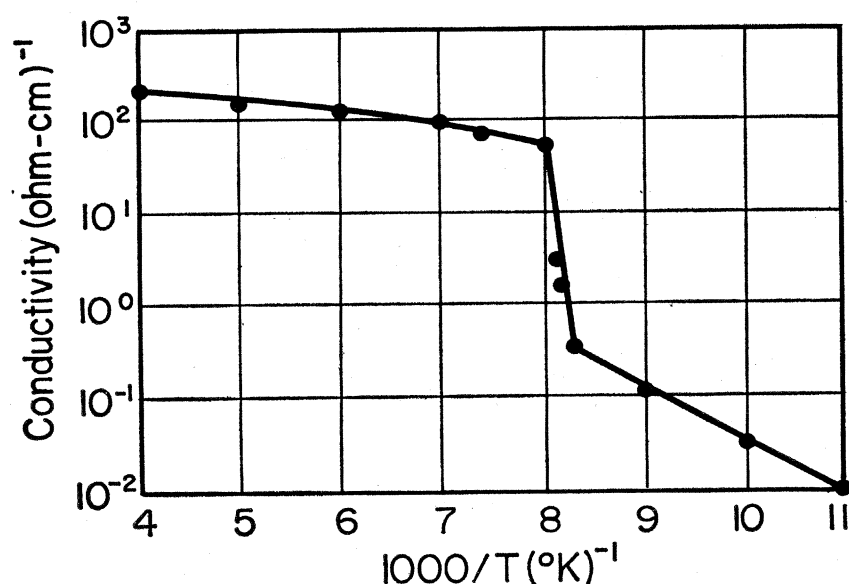
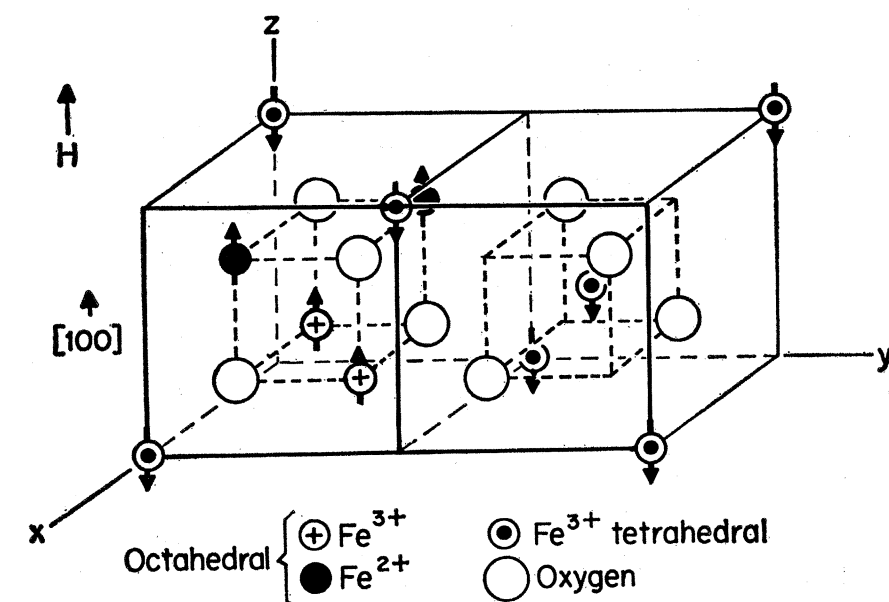


Fig. 25. Freezing-in of order in magnetite.

tolerance conditions: carbon atoms (group IV of the periodic system, Fig. 3) can be replaced by 50 percent each of boron atoms (group III) and of nitrogen atoms (group V) without destroying the structure of the benzene ring or the diamond lattice. Here the electron-cloud structure can average over the nuclear charge distribution. However, if we try to stretch the limits of symmetrical replacement further by introducing the atoms beryllium (group II) and oxygen (group VI) instead of boron and nitrogen, the benzene ring equivalent, beryllium trioxide, does not form and the beryllium oxide crystal does not derive from the diamond structure.

A comparison of the two crystal types boron nitride and beryllium oxide yields more information (Fig. 21): the diamond lattice, when composed of two different types of atoms, is identical with the sphalerite structure (zinc blende); the beryllium oxide lattice, with the wurtzite structure of zinc sulfide. The former can be derived from two interpenetrating cubic close-packed lattices; the latter, from two hexagonal ones. Hence, by increasing the polarity of the array, we have unbalanced the sphalerite in favor of the wurtzite arrangement. In both situations each atom type is tetrahedrally bonded to the other (CN 4), but, viewed in the [111] direction, subsequent tetrahedra in sphalerite are staggered and in wurtzite, eclipsed. The staggered array allows better space accommodation; the eclipsed array, a closer bonding of opposite charges. This explains the transformation observed.

The extreme step in polar substitution is balancing of lithium (group I) against fluorine (group VII). This wipes out the tetrahedral (CN 4) organization of the zinc sulfide lattices in favor of the octahedral (CN 6) coordination of the rock salt structure. The change has been enforced by the increase in radius ratio of cation to anion (r_c/r_a for $\text{Be}^{++}/\text{O}^{--} = 0.25$; for $\text{Li}^+/\text{F}^- = 0.52$) as would be expected from Fig. 11. Still, like the sphalerite structure of boron nitride, the rock salt structure of lithium fluoride can be derived from two interpenetrating cubic close-packed sublattices (see Fig. 6).

This switching between crystal types (derived from close-packed arrays) at the command of tolerance conditions concerned with polarity and space accommodation invites clarification of the kinship of such types. Insight is provided by viewing the interstitial space

arrangement for the close-packed structures of Fig. 4. This space is partitioned into interlocking tetrahedral and octahedral compartments (Fig. 22); a lattice section of n atoms contains n octahedral and $2n$ tetrahedral sites. The centers of the octahedra lie halfway between the layers of the original lattice; those of the tetrahedra, at $\frac{1}{4}$ and $\frac{3}{4}$ of the spacing. [A model design with transparent tetrahedral and octahedral building blocks has recently been perfected by A. Loeb in connection with his imaginative approach to a new crystal algebra (17).]

Starting with a cubic-face-centered array of layer sequence ABCABC . . . , we arrive at the rock salt structure by occupation of all the octahedral interstitial sites (see Fig. 6) or at the sphalerite structure by filling of all tetrahedral sites in either the $\frac{1}{4}$ or the $\frac{3}{4}$ location. By choice of the hexagonal close packing with layer sequence ABAB . . . and occupation of one of the two sets of tetrahedral sites, the wurtzite structure is created (see Fig. 21). Since the centers of the octahedra lie midway between the original layers, the spacing between the positive and negative planes of the rock salt structure is uniform and the crystal has a center of symmetry. For the tetrahedrally bonded sphalerite and wurtzite, on the other hand, the occupation of the $\frac{1}{4}$ or $\frac{3}{4}$ center positions causes a periodic bunching of the charged planes; the center of symmetry is destroyed.

Structure and Properties

Such topological differences in competing arrangements should produce profound property changes. Indeed, crystals of the rock salt structure remain electrically neutral under mechanical stress; insulators of the sphalerite type react piezoelectrically (that is, they create potential differences of opposite signs on tension and compression), while those of the wurtzite type are in addition pyroelectric (potential differences of opposite signs develop also on heating and cooling). Thus, both tetrahedrally bonded polar crystal types can serve as electromechanical transducers, and the wurtzite type can serve in addition as a thermosensing device.

For molecular interpretation of these phenomena, the ions of opposite polarity can be visualized as forming a network of permanent dipole moments. In

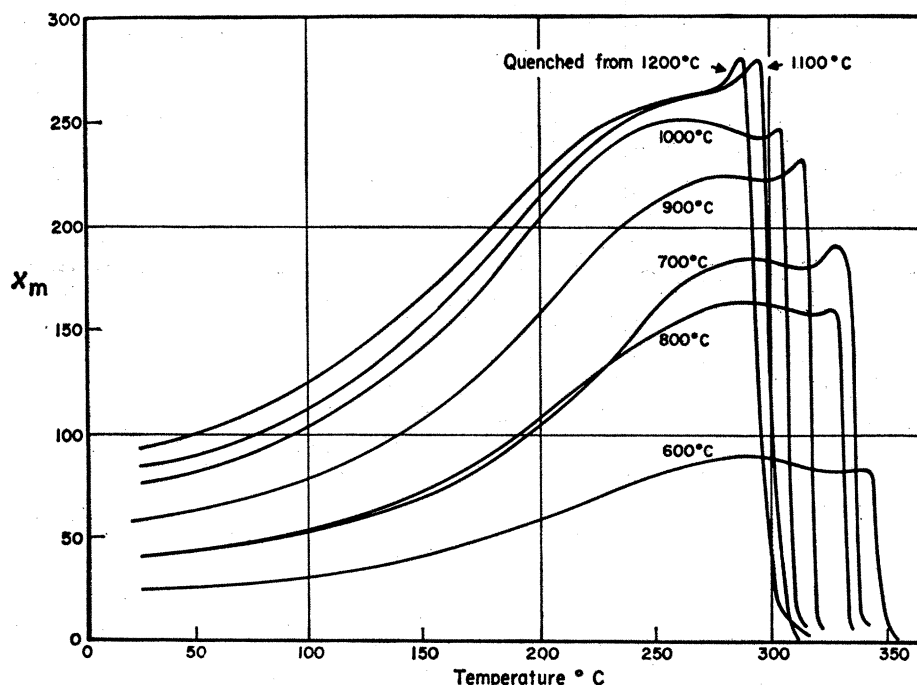


Fig. 26. Freezing-in of disorder in magnesium ferrite.

the rock salt structure the neutralizing balance of these moments cannot be upset by mechanical distortion; in sphalerite it can be, and in wurtzite it does not exist a priori, because the moments do not cancel but create a polar axis.

The polar double-layer structure produces additional differences between the $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ directions in sphalerite, and between the $[001]$ and $[00\bar{1}]$ directions in wurtzite; the x-ray scattering is dissimilar in the two opposite directions, and since the crystals terminate on the one site with a cation and on the other with an anion layer, the electrochemical potentials and etching properties of these end surfaces are quite dissimilar (Fig. 23) (18). By combining sphalerite and wurtzite in twinned arrays, high-voltage photocells can be produced (19).

The structure transformation observed for the sequence of insulators $C \rightarrow BN \rightarrow BeO \rightarrow LiF$ in the second row of the periodic system repeats itself for the b elements of the higher rows (silicon, germanium, and gray tin) in the corresponding group III-V (20), group II-VI, and group I-VII compounds (21). These elements and compounds are the decisive semiconductor materials for transistors and solid-state diodes, for thermoelectric converters, and for solar-energy photocells. Here the band structure, the gap width between valence and conduction band, the mass and mobility of electrons and holes can be adjusted by composition changes, and charge carriers can be mobilized by

cation substitution in minute quantities (doping). An impressive amount of fundamental molecular-science knowledge has been gathered rapidly about these materials under the impact of molecular-engineering applications (21).

The same is true for the ferrites (22), the semiconductors indispensable for magnetic high-frequency applications (memory devices, gyrators, and so on). Again the model of a close-packed array with interstitial sites (Fig. 22) helps to explain basic properties. Magnetite, the prototype ferrite (Fe_3O_4) is formed—in ionic description—by a cubic close-packed O^{2-} sublattice; one eighth of its interstitial tetrahedral sites are occupied by Fe^{3+} ; one half of its octahedral sites, by Fe^{3+} and Fe^{2+} cations in a 1:1 ratio. The cations in this inverse spinel structure (Fig. 24) are so placed that the electrostatic repulsion is minimized. Since Fe^{2+} and Fe^{3+} cations in equal number occupy equivalent octahedral interstices, easy electron exchange between them makes magnetite too conductive for most purposes. The material can be transformed into an insulator by cation substitution that blocks this electron transfer.

The unpaired electrons in the cations of the transition elements are the carriers of the magnetic moments in the ferrites. Electron exchange between Fe^{2+} (four Bohr magnetons) and Fe^{3+} (five Bohr magnetons) varies the magnetic arrangement at the same time. This coupling between electric and mag-

netic properties becomes clearly visible in magnetite by freezing-in an ordered sequence of Fe^{2+} and Fe^{3+} below -155°C . The conductivity drops by several orders of magnitude, and if the magnetic spins are ordered by application of an external field during cooling through the transition, a magnetic axis is frozen-in, altering the hysteresis loop completely (5, 23) (Fig. 25). Conversely, since in the ferrites only a fraction of the interstitial sites are occupied, high temperature extends the spread of cations to less favorable positions. In consequence, by quenching-in such disorder, the magnetic properties can be greatly affected (Fig. 26).

These examples must suffice. They show that the connection between structure and properties can be of obvious directness and, in other situations, buried in prehistory effects which challenge the tenacity of a psychoanalyst for their elucidation. The principal reasons for complications are the same as in living systems: a macroscopic phenomenon may be produced by a variety of molecular causes; furthermore, the phenomenon may be related not to the ideal structure of a material but to the faults built into such a structure.

Science in previous times believed that "nature loves simplicity" and that man in his incredible complexity presents a "mighty effort contrary to nat-

ure." Dictatorships enslaving man could thus be justified as a return to nature's order. Today, this excuse of tyrants has vanished. Every day we learn with increasing insight that nature is incredibly complex and that man is one incident in its organization. At the outset we raised the question: What shall we most reasonably do with our natural resources? Molecular designing allows us to realize Jules Verne's fantasies. The answer is therefore not any longer what we can do, but what we want to do. Molecular science and molecular engineering must operate as allies of social science and political statesmanship in imaginative planning for the most beneficial transformation of the world's resources.

References and Notes

1. H. A. Meyerhoff, "Changing concepts of mineral raw materials in the national economy," paper presented at the 128th meeting of the AAAS, Denver, 1961.
2. H. Brown, "Science and government," paper presented at the 128th meeting of the AAAS, Denver, 1961.
3. The work reported in this article was made possible through support extended to the Massachusetts Institute of Technology jointly by the Navy Department (Office of Naval Research), the Army Signal Corps, and the Air Force, under ONR contract Nonr-1841 (10), NR-018-801; also by the Air Force under contract AF 33 (616)-8353. I am greatly indebted to my co-workers C. W. Nelson and J. J. Mara for help in preparing the figures.
4. See, for example, J. L. Greenstein, *Am. Scientist* **49**, 449 (1961).
5. See, for example, A. von Hippel, *Molecular*

- Science and Molecular Engineering* (Massachusetts Institute of Technology Press and Wiley, New York, 1959).
6. See L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, ed. 3, Ithaca, 1960).
 7. See, for example, J. C. Slater, in *Handbuch der Physik*, S. Flügge, Ed. (Springer, Berlin, 1956), p. 1.
 8. A. von Hippel, *J. Chem. Phys.* **16**, 372 (1948).
 9. A. S. Balchan and H. G. Drickamer, *ibid.* **34**, 1948 (1961).
 10. See *Progress in Very High Pressure Research*, F. P. Bundy, W. R. Hibbard, Jr., H. M. Strong, Eds. (Wiley, New York, 1961).
 11. *Sci. Am.* **205**, No. 9 (1961).
 12. L. W. Tilton, *J. Res. Natl. Bur. Std.* **59**, 139 (1957).
 13. J. Bischof and B. E. Warren, *J. Am. Chem. Soc.* **21**, 287 (1938).
 14. A. H. Silver and P. J. Bray, *J. Chem. Phys.* **29**, 984 (1958).
 15. S. D. Stookey, in *Ceramic Fabrication Processes*, W. D. Kingery, Ed. (Massachusetts Institute of Technology Press and Wiley, New York, 1958), p. 189.
 16. W. N. Lipscomb, in *Advances in Inorganic Chemistry and Radiochemistry*, H. J. Emeleus and A. G. Sharpe, Eds. (Academic Press, New York, 1959), vol. 1, p. 117; —, A. R. Pitochelli, M. F. Hawthorne, *J. Am. Chem. Soc.* **81**, 5833 (1959); J. A. Wunderlich and W. N. Lipscomb, *ibid.* **82**, 4427 (1960); E. B. More, Jr., L. L. Lohr, Jr., W. N. Lipscomb, *J. Chem. Phys.* **35**, 1329 (1961).
 17. A. L. Loeb, *Acta Cryst.* **11**, 469 (1958); I. L. Morris and A. L. Loeb, *ibid.* **13**, 434 (1960).
 18. H. C. Gatos, *Surface Chemistry of Metals and Semiconductors* (Wiley, New York, 1960), p. 399.
 19. W. J. Merz, *Helv. Phys. Acta* **31**, 625 (1958).
 20. H. Welker and H. Weiss, in *Solid State Physics*, F. Seitz and D. Turnbull, Eds. (Academic Press, New York, 1956), vol. 3, p. 1.
 21. See, for example, "Semiconductors," *American Chemical Society Monograph Series* (1959); *J. Appl. Phys.* **32**, No. 10 (1961).
 22. See, for example, J. Smit and H. P. J. Wijn, *Ferrites* (Wiley, New York, 1959).
 23. B. A. Calhoun, *Phys. Rev.* **94**, 1577 (1954).

Cell Disruption by Ultrasound

Streaming and other activity around sonically induced bubbles is a cause of damage to living cells.

D. E. Hughes and W. L. Nyborg

Ultrasonic methods for injuring or disrupting microorganisms or animal cells in vivo are now widely used (1, 2), but there is as yet no generally accepted theory to explain their disruptive effects (3). In connection with fragmentation of microorganisms in suspension, it is an accepted view that a major role is played by a sonically maintained activity known as "gaseous cavitation."

This activity occurs in liquids containing dissolved gases and takes place especially readily in the presence of solid or quasi-solid surfaces containing tiny cracks or crevices. These surfaces may be presented by the vessel walls, or by tiny particles suspended in the liquid. Alternations of pressure in the sound field cause bubbles (containing gas or vapor, or both) to grow and take part

in a complex and extremely energetic motion. Noltingk and Neppiras (4) have shown that under suitable conditions a tiny pocket of air of, say, a few microns in radius expands to a size thousands of times greater than the original volume, then violently collapses to a fraction of the original size, all within a time less than that for one cycle of the sound. In the collapse phase Noltingk and Neppiras predict instantaneous temperatures of the order of 10^4°K and pressures of the order of 10^6 atmospheres. The equations for such nonlinear behavior of the bubbles have recently been developed further by Flynn (5). Among the effects attributed to cavity collapse are local heating and electrical discharges, sonoluminescence, chemoluminescence, and free radical formation (6, 7).

Dr. Hughes, a member of the Medical Research Council, Unit for Cell Metabolism Research, department of biochemistry, Oxford, England, is at present visiting professor in the department of microbiology, Dartmouth Medical School, Hanover, N.H. Dr. Nyborg is professor of physics at the University of Vermont, Burlington.