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THE CHEMICAL BOND AND SOLID-STATE PHYSICS

A new scale of ionicity, with which the ionic character of bonding in crystals can be predicted and measured, has led to improved understanding of such crystalline properties as lattice structure, heats of formation, elastic constants and nonlinear optical properties.

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ADVANCES in quantum chemistry, as in any other field, need novel concepts to keep pace with the great increase in available experimental data and theoretical understanding. The concept of ionicity of the chemical bond is an example. For 35 years Linus Pauling's development of a definition of ionicity, based on heats of formation of binary crystals, was standard. Here I will describe a new definition of ionicity, derived from spectroscopically obtained transition energies between bonding and antibonding states of semiconductor crystals, and show how it compares with the older one.

Soluble and insoluble problems

The layman's picture of theoretical physics is one of beautiful, complete mathematical laws that supply an exact and immutable description of nature. To counteract such naiveté we should remember that each subject is salted with insoluble, although apparently simple, problems. In classical mechanics there is the three-body problem; in quantum mechanics almost no problem is analytically tractable. Indeed only a few problems, such as the hydrogen atom and the harmonic oscillator, are both interesting and analytically soluble. From these limitations grow some of the most important theoretical problems of modern physics.

Thermodynamics and statistical mechanics were developed to avoid the limitations of the classical many-body problem. The abstract structure of these disciplines is well understood; they provide the basis of classical chemistry. Similarly, to avoid the analytic limitations of wave mechanics, it was once believed that giant computers were all that was needed. These computers have now arrived, but they have not brought the millenium. The results obtained from computer calculations, although valuable in themselves, can not supply the abstract concepts needed for quantum chemistry. We need such concepts so that we can understand important consequences of the wave motion of many electrons in terms of the chemical bond, much as thermodynamics enables us to understand observable features of the classical motion of many particles in terms of entropy and temperature.

Today many sophisticated theorists have concluded that it is not possible to characterize the chemical bond in this fashion. I believe that such a characterization is possible, and that the first correct steps in this direction have already been taken.

It is typical of an emerging field that there is controversy not only about results but to an even greater extent about goals. For example, in the 18th century the average person thought of bodies as hot or cold. Perhaps a few persons were sophisticated enough to realize that "heat content" was not well defined. Only after the second law of thermodynamics had been formulated in terms of the cyclic properties of ideal gases, however, did it become apparent that the concept of heat content could be usefully altered in such a way as to make it a precise tool.

Prior to the formulation of the second law one could justifiably argue that real heat engines, although of great practical utility, were not of fundamental interest because they could not be described in mathematical terms. Thus all quantitative progress could be supposed to depend on the development of such mathematical tools as Green's functions. Plus ça change, plus c'est la même chose.

Simple concepts

The everyday tool of modern structural chemistry is the chemical bond. Perhaps more widely and more successfully than any other one person, Pauling has argued[1] that the nature of the chemical bond can be understood quantitatively in terms of simple concepts such as *covalency, ionicity*, standard *bond lengths* and *bond angles, resonance*, and so on. When Pauling demonstrated that the bond length of the C–C bond was the same to within 1% in diamond and in many hydrocarbon molecules, it appeared that his hopes for a quantitative theory were indeed well founded.

The passage of time has seen the experimental confirmation of many of Pauling's ideas, but paradoxically it has also dimmed the early optimism. Only one major theoretical contribution to Pauling's program has appeared in the 35 years since its publication. At least in the simple case of the Hückel theory of π levels of aromatic hydrocarbons, C. A. Coulson found a mathematical formulation of the qualitative concept of resonance. Indeed Coulson showed that for homopolar bonds one could generalize the notion of single, double and triple bonds to yield a nonintegral measure of bond strength called *bond order*. He proposed a linear relationship between bond length and bond order (figure 1) that has since been borne out to 10^{-11}cm by electron-diffraction experiments. Coulson's theory of C–C bond lengths has been described[2] as "one of the most satisfactory predictions of molecular orbital theory."

There is a lesson to be learned from this example, and in the age of the giant computer it is one well worth emphasizing. The concept of bond order, at once so simple and yet so general, was not derived from the accurate numerical variational solution of the Schrödinger equation for a small number of unrelated small molecules. Rather it emerged from a simplified theory of the chemical bond in the most extensive known system of large molecules—the aromatic hydrocarbons. In considering such a sys-

DEFINITION OF SYMBOLS

A^NB^M—A binary crystal composed of elements A and B with N and M valence electrons per A and B atom respectively.

F_i^4—Maximal ionicity of four-fold coördinated crystals.

F_i^6—Minimal ionicity of six-fold coördinated crystals.

D_{AB}—The average heat of formation of an AB bond in crystals or molecules.

X_A—A dimensionless number that defines the electronegativity of element A, which is defined by Pauling as the power of an atom to attract electrons to itself. In practice one is usually concerned only with electronegativity differences, for example, $X_A - X_B$.

f_i (A,B)—A number lying between zero and unity that measures the ionicity of the bond, that is, the fraction of time the valence electrons spend in the configuration A^+–B^- compared to A : B.

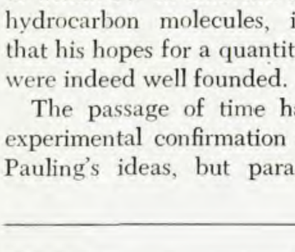
E_h—The average energy gap between bonding and antibonding energy levels (contributed by covalent forces).

C—The average energy gap between bonding and antibonding energy levels (contributed by ionic forces).

E_g—The total energy gap contributed by both covalent and ionic forces.

ϵ_0 (AB)—The electronic dielectric constant of an AB crystal, equal to the square of the low-frequency limit of the optical index of refraction n(AB).

R_A—The number of the row of the periodic table that contains element A.



James C. Phillips took his PhD in 1956 at the University of Chicago. After two years at Bell Telephone Laboratories, a year at Berkeley and a year at the Cavendish Laboratory, he joined the physics faculty at Chicago. As an Alfred P. Sloan fellow he revisited Cambridge in 1963 and 1967. He became a full professor at Chicago in 1965, and in 1968 he rejoined the theoretical-physics department at Bell Labs.

BACKGROUND

Two atoms A and B are said to be **chemically bonded** when the forces acting between them are sufficiently strong to form a stable aggregate at temperatures of interest. The **covalent bond** involves sharing between the atoms of an even number of valence electrons, two per single bond. A multiple bond involves sharing $2n$ electrons, where $n > 1$ is the total **bond order;** $n - 1$ is often called the π bond order.

Generally in an A–B bond some electronic charge is transferred from A (the cation) to B (the anion). The bond is then said to be partly **ionic** (A^+–B^-) and partly **covalent** (A : B). This separation is sometimes described quantum-mechanically as the superposition of ionic and covalent wave-function amplitudes. The valence electrons would then, probabilistically speaking, spend part of the time in the ionic state and part of the time in the covalent one. Such alternation is often called **resonance,** in analogy with a harmonic oscillator, which alternately stores its energy in kinetic and potential terms. One may also have resonance between single and multiple bonds, in which case n can be nonintegral.

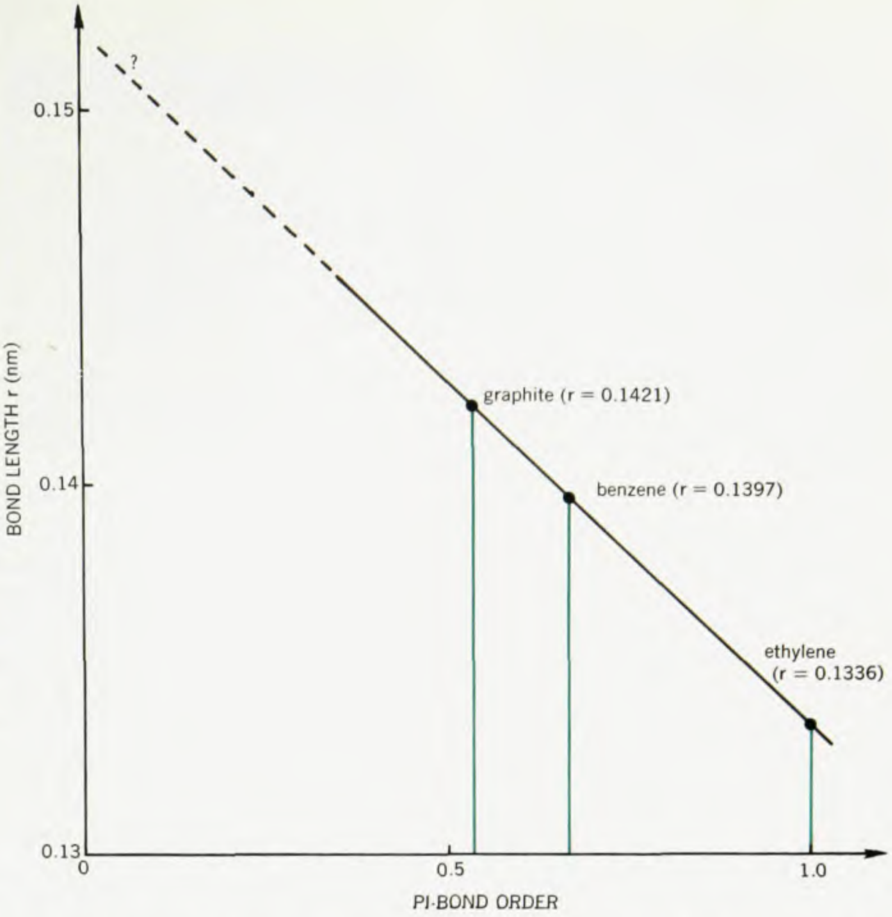
tem Coulson was forced to seek mathematical invariants, rather than isolated numbers that could be used to describe particular cases.

During the 1930's many efforts were made to apply the experience obtained from the wave mechanics of atoms to other systems. Thus arose nuclear-shell theory, the cellular theory of metals, and molecular-orbital theory. Molecules, with their loose packing of atoms, represent the system closest to isolated atoms; so, not surprisingly, they showed the most rapid progress. (For example, the modern theory of the ultraviolet spectra of hydrocarbons was already delineated by E. Clar in the 1930's.) Slow progress in nuclear theory was to be expected, but the results for quantum theory of crystals were surprisingly poor. The cellular method proved suitable only for two or three alkali metals, and other methods involved elaborate computations beyond the reach of most workers.

Semiconductors

The quantum theory of crystals has developed rapidly in the last ten years. The popular view attributes this progress to the giant computers, but I do not entirely accept this explanation. Those who have followed the field closely realize that elaborate calculations have in nearly every case merely succeeded in embellishing theoretical pictures derived from simpler models and experiment. This has been true both for Fermi surfaces of metals[3] and for energy bands of semiconductors.[4]

Semiconductors form, of course, the technological backbone of modern solid-state physics, just as the aromatic hydrocarbons do for organic chemistry. Nearly 40 crystals of formula A^NB^{8-N} (that is, with eight s–p valence electrons per atom pair) have tetrahedrally coördinated structures. Twenty of them have been produced in the form of large single crystals suitable for precise experimental studies. Together with the rock-salt or NaCl-type crystals (which also have face-centered cubic space groups) this family is by far the largest one of homologous structures. Its optical spectra are now understood in far greater detail than those of aromatic hydrocarbons, and not unexpectedly the energy levels are also known with much greater completeness. Indicative of the present level of understanding is the title of a recent paper[5]: "Band Structures . . . for Fourteen Semiconductors . . ." (As recently as 1961 we were not certain of the energy bands of silicon and germanium!)



COULSON'S RELATION between bond length and bond order for the carbon–carbon bond. This linear relation represents the concept of resonance. —FIG. 1

When a major breakthrough of these proportions occurs, theoretical physicists find that they can say something significant about the basic principles of chemistry. Those familiar with semiconductor physics have noted that, after World War 2, the crystals A^NB^{8-N} with $A = B$ and $N = 4$ first received the most attention, then those with $N = 3$, then $N = 2$, and so on. In other words, before the war, ionic crystals such as Cu_2O were employed in devices; after the war, covalent crystals were discovered to be more useful, and recent developments have brought in the partially ionic crystals only gradually.

These historical remarks suggest that the family of A^NB^{8-N} semiconductors should represent the ideal case for putting the concept of ionicity on a firm quantitative footing, just as the aromatic hydrocarbons did for the concept of resonance. This supposition has indeed proved to be the case. To understand how it happened, however, one must first define what one means by a *scale*, and then explain what one means by a *true scale*.

Temperature scales

Consider again the question of heat. Temperature must be measured by a thermometer. Any physical property that establishes a one-to-one correspondence between temperature and an observable can be made the basis of a thermometric scale. For example, so long as the coefficient of thermal expansion of a material is positive, the length of a rod of that material determines a thermometric scale.

A general thermometric scale, although convenient for calibration, serves no other purpose. A *true scale*, however, describes one property of an ideal system and, at the same time, *predicts* the behavior of an apparently independent property. Such a scale embodies a physical law, and as such it must (as the name "true" implies) be unique. (Any

	GROUP IA				GROUP IB	
	Li	Na	K	Rb	Cu	Ag
F	6	6	6	6	4	6
Cl	6	6	6	6	4	6
Br	6	6	6	6	4	6
I	6	6	6	6	4	4

	GROUP II A			GROUP II B				
	Ca	Sr	Ba	Be	Mg	Zn	Cd	Hg
O	6	6	6	4	6	4	6	6
S	6	6	6	4	6–4	4	4	6–4
Se	6	6	6	4	6–4	4	4	4
Te	6	6	6	4	4	4	4	4

COORDINATION NUMBERS for $A^N B^{8-N}$ crystals for $N = 1$ (on the left) and $N = 2$ (on the right). Thus NaCl has a coördination number of 6, and ZnO has a coördination number of 4. The problem of predicting these numbers, which is essentially that of predicting the crystal structure, was traditionally insoluble. —FIG. 2

other true scale could be related to it, because the physical laws involving this variable are all connected.) In the thermometric case the true scale is the Kelvin or absolute temperature scale, defined, for example, by the pressure of an ideal gas at fixed density. According to the second law of thermodynamics, the Kelvin scale is the true one because the reciprocal of the Kelvin temperature functions as an integrating factor for heat exchange.

Ionicity scales

Next we need the same kind of scale to describe the ionicity of the chemical bond. Given several such proposed scales, one can test their accuracy and also look for an independent way to measure the accuracy of ionicity scales that is free of semantic ambiguity.

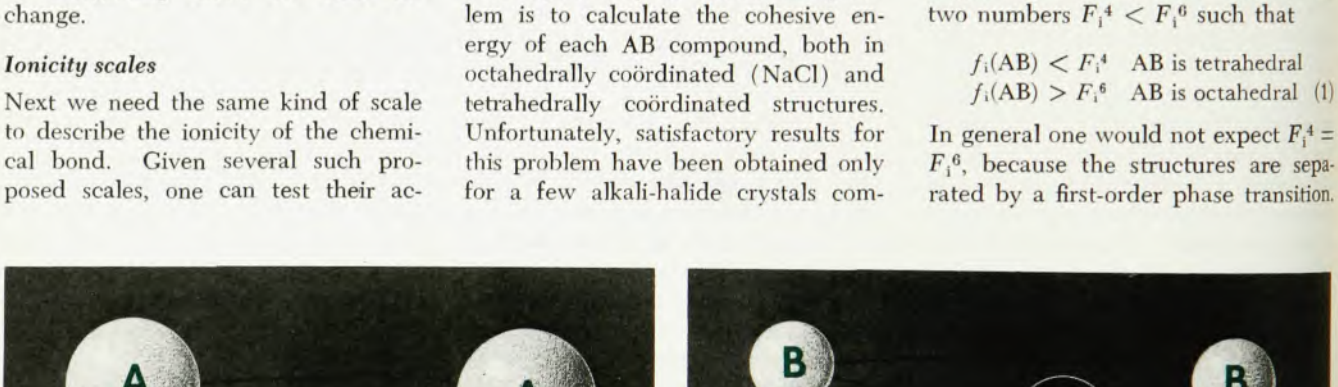
One objective test consists of examining a traditionally insoluble problem, the problem of predicting the crystal structure (or atomic coördination number) of the $A^N B^{8-N}$ crystals. These numbers are shown in figure 2 for $N = 1$ and $N = 2$.

A logical way to attack this problem is to calculate the cohesive energy of each AB compound, both in octahedrally coördinated (NaCl) and tetrahedrally coördinated structures. Unfortunately, satisfactory results for this problem have been obtained only for a few alkali-halide crystals composed of light (and therefore low polarizability) ions. All calculations (even the purportedly quantum-mechanical ones) follow the pattern, originated by Max Born and elaborated by Joe Mayer, based on the assumption of localized valence electrons whose interactions are calculated using the multipole expansion of classical electrostatics. This expansion fails to treat covalent effects associated with electron sharing, and therefore it cannot explain the occurrence (even for $N = 1$) of tetrahedrally coördinated $A^N B^{8-N}$ crystals. For this reason, with the cohesive-energy approach no one has been able to predict successfully whether a given compound will be octahedrally or tetrahedrally coördinated.[6]

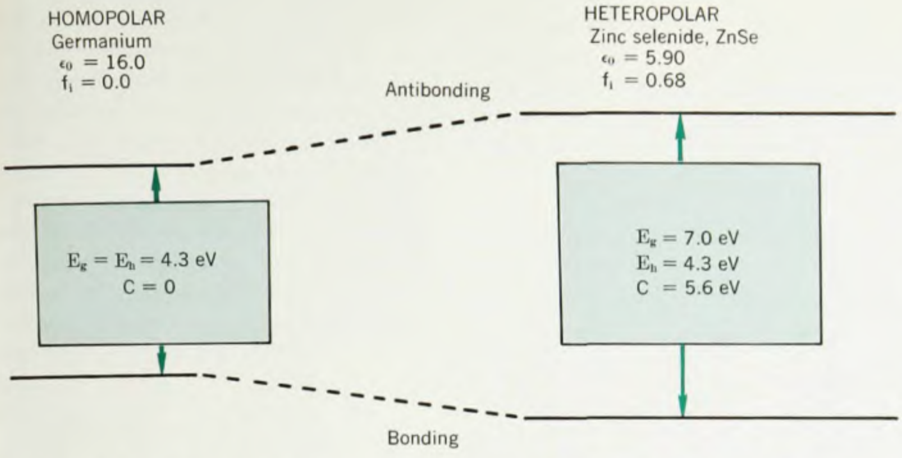
The NaCl structure is certainly predominantly ionic, and the diamond structure is the prototype of all covalent structures. (Its tetrahedral coördination is explained by Pauling in terms of sp^3-hybridized bonds.) Therefore, given an ionicity scale that specifies fractional ionicity $f_i = f_i(AB)$ for each AB compound, we might expect that there would exist two numbers $F_i^4 < F_i^6$ such that

$$\begin{aligned} f_i(AB) &< F_i^4 \quad \text{AB is tetrahedral} \\ f_i(AB) &> F_i^6 \quad \text{AB is octahedral} \end{aligned} \qquad (1)$$

In general one would not expect $F_i^4 = F_i^6$, because the structures are separated by a first-order phase transition.



DIRECTED-VALENCE ORBITALS. On the left (a) are bonding orbitals, and on the right (b), antibonding orbitals. The A atoms are more electropositive, the B atoms more electronegative. The bonding orbitals have the lower energy because they are directed towards their nearest neighbors and also because they are centered predominantly on the more electronegative atom. These two contributions to the bonding–antibonding energy gap are called E_h and C, respectively. (See also figure 4.) —FIG. 3



ENERGY GAPS E_h and C shown for two examples: germanium (homopolar) and zinc selenide (heteropolar). In the elemental structure (such as diamond and germanium, the example shown), $C = 0$ and $E_g = E_h$. That is, the entire energy gap arises because the bonding orbitals are directed towards their nearest neighbors, whereas the antibonding ones are directed away. However, for a II–VI crystal such as our example, ZnSe, C may be larger than E_h. Then the energy gap is largely the result of the bonding states being centered predominantly on the more electronegative atoms; the antibonding states are centered on the more electropositive sublattice. —FIG. 4

For simplicity, however, we shall assume for the moment that $F_i^4 = F_i^6 = F_i$.

Most of the ionicity scales that have been proposed so far contain intrinsic inaccuracies. In each case there is *no* value of F_i that successfully predicts the coördination configuration of all of the approximately 40 tetrahedrally coördinated and approximately 30 octahedrally coördinated $A^N B^{8-N}$ crystals. This difficulty suggests a procedure: for each definition of F_i we calculate the number of wrong predictions, $N = N(F_i)$, as a function of F_i, and obtain the minimal value $N_0 = N(F_i^0)$ at the best choice of F_i^0 for that definition of F_i.

What is the par score?

To obtain an idea of what constitutes a par value of N_0, imagine for a moment that we confront a clever high-school student with our list of 70 crystals, telling him that the crystals may be divided into two groups, 40 being "covalent" like C_2 (diamond) and 30 being "ionic" like NaCl. We also give him a copy of the periodic table. Being experienced at multiple-choice tests, he immediately notices that if he lists all the crystals with the cation from column IA (alkali) or column IIA (alkaline earth) as ionic, he gets about the right number in each group. This classification makes nine errors, but it uses no free parameters and no knowledge other than that contained in the periodic table itself. Thus $N_0 = 9$ is par for the exam.

Pauling's definition of ionicity

It would be interesting to see how various definitions of ionicity meet this test, but I have space only for a detailed discussion of Pauling's definition[1] and a recent definition based on dispersion theory.[7] Pauling's definition goes as follows:

Consider the heats of formations of A–A, B–B and A–B bonds. Generally in molecules the energy D_{AB} of the heteropolar A–B bond exceeds the average of the energies D_{AA} and D_{BB} of the homopolar A–A and B–B bonds. According to Pauling this extra energy is ionic in origin, and it arises by transfer of electrons from the less electronegative to the more electronegative atom. Thus he defines elemental electronegativities X_A and X_B by the relation

$$D_{AB} - (D_{AA} + D_{BB})/2 \propto (X_A - X_B)^2 \quad (2)$$

The constant of proportionality is chosen to have the dimensions of energy, so that X_A and X_B are dimensionless and increase by 0.5 with valence change $\Delta Z = 1$ for the first row of the periodic table. Fractional ionic character is defined by

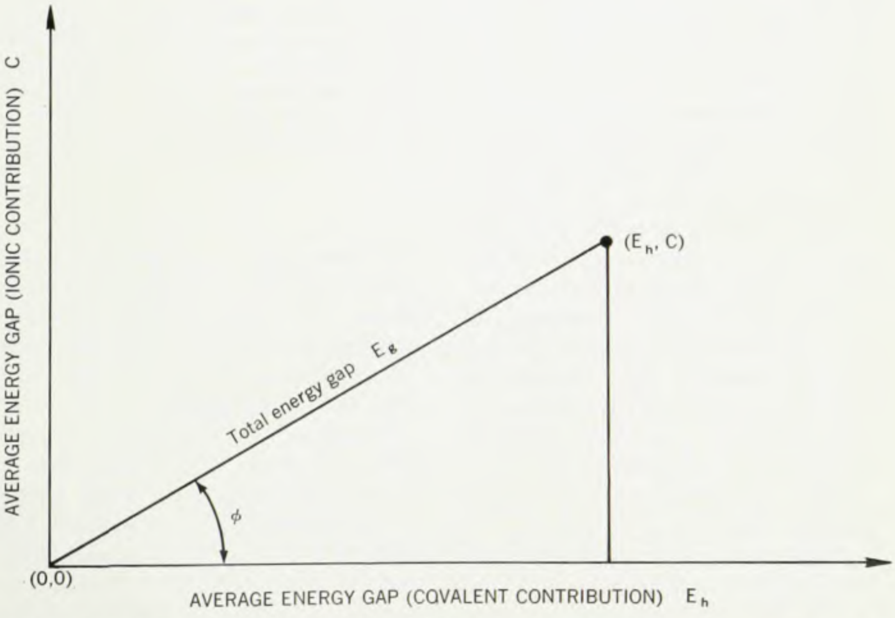
$$f_i(A,B) = 1 - \exp[-(X_A - X_B)^2/4] \quad (3)$$

There are several disturbing features of Pauling's definitions—our equation 2 and equation 3. The specific functional form of equation 3 appears to have been chosen merely for convenience, and it satisfies only the weak conditions

$$0 \leqslant f_i < 1 \quad (4)$$

$$f_i(A,B) = f_i(B,A) \quad (5)$$

which can also be met by many other definitions. It appears unlikely that, even if equation 2 is accurate, equation 3 would produce a true scale.

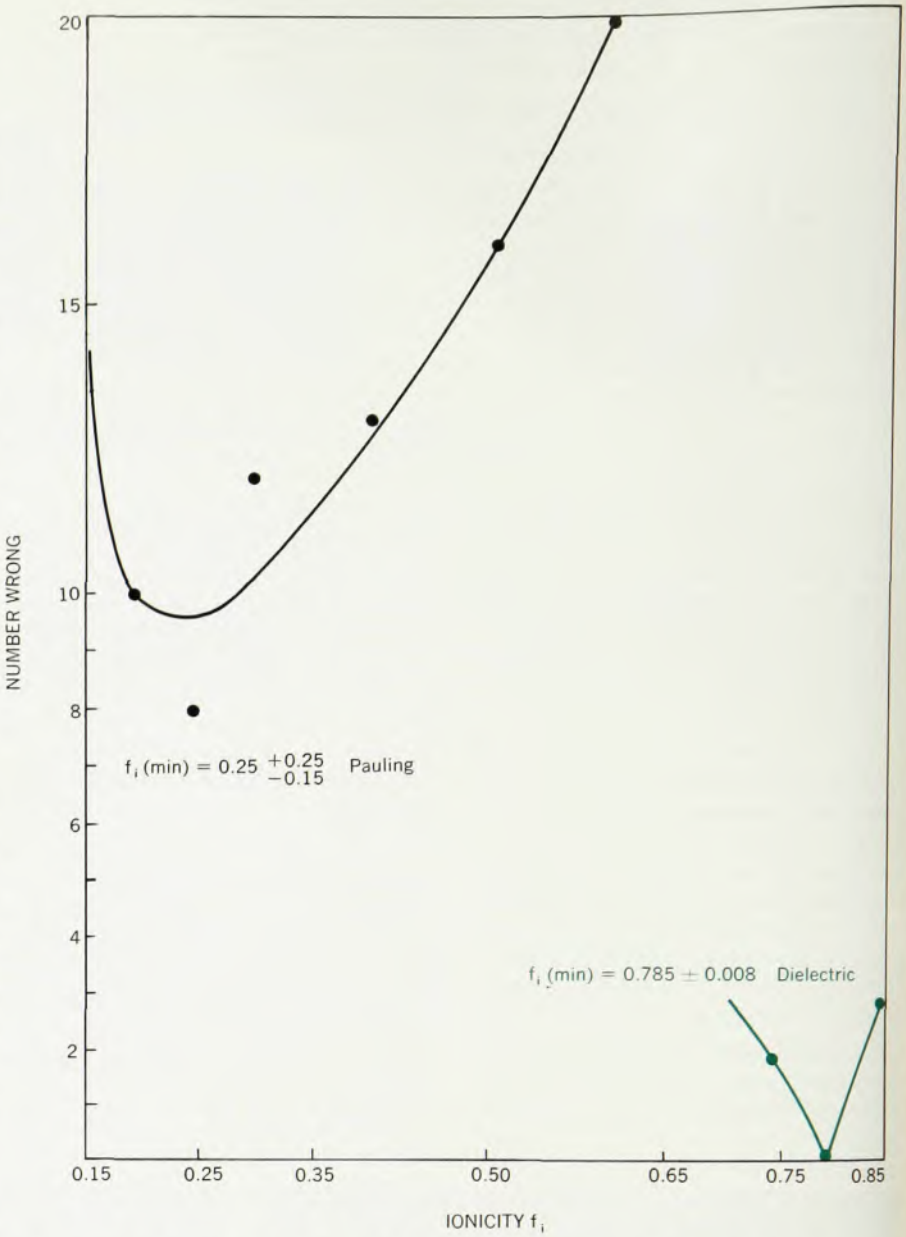


GEOMETRICAL CONSTRUCTION to define the ionicity phase angle ϕ in the (E_h, C) plane. —FIG. 5

More likely the scale has built-in distortions similar to those of real thermometers compared to ideal gases.

But can equation 2 be accurate? After all, *there is no universal constant* with the dimensions of energy. (Some of my colleagues have suggested that the Rydberg is such a constant. Of course, it is not; the Rydberg represents the binding energy of an electron in a certain potential expressed in terms of universal constants e, $h/2\pi$ and m, which are independent of that potential.) Therefore the constant of proportionality used by Pauling must represent some average bond energy. But this constant may well depend on the rows of the periodic table R_A and R_B to which A and B belong in quite a different way for different pairs—that is, it is not really constant. And, because $(X_A - X_B)^2$ enters both equation 2 and equation 3, this question is inextricably related to the definition of ionicity.

It is at this point that many quantum theorists decided that "ionic character of a bond," like heat content, is something that can not be precisely defined. However, just because a particular mathematical formulation fails, one is not justified in concluding that the original ideas are unsound. Just as entropy replaces heat content, so a better mathematical formulation may make ionic character well defined.



STATISTICAL TEST of the two definitions of ionicity, in terms of their success in predicting whether the crystal A^NB^{8-N} will have a four-fold or six-fold coördinated structure (figure 2). There are more than 70 such crystals. Here Pauling's score is in black, that derived from the dielectric definition of ionicity in color. Error limits on f_i(min) have been established by determining the excursion in the critical ionicity required to more than double the number of incorrect predicted structures. —FIG. 6

A better definition

How would such a better formulation proceed? First we must recognize, as did Pauling, that the energy of an A–B bond contains two parts—a homopolar, or covalent, part and a heteropolar, or ionic, part. Second, we recognize that one can define these energies much more accurately spectroscopically, in terms of transition energies between bonding and antibonding states, than one can by heats of formation. (Heats of formation always involve changes in structure, and hence they involve not only changes in bond energies, but changes in bond–bond interaction as well, and these we wish to avoid.) Detailed spectroscopic information was not available when Pauling formulated the problem.

These states are represented by directed-valence orbitals, as sketched for tetrahedral coördination in figure 3. The bonding states have lower energy, are centered predominantly on the more electronegative atom, and point towards the nearest-neighbor atoms. The antibonding states are centered predominantly on the more electropositive atom, and point away from the nearest neighbors.

To identify the homopolar energy spectroscopically, one notices that it can depend only on the bond length or nearest-neighbor distance d. A striking feature of tetrahedrally coördinated crystals A^NB^{8-N} is that if $R = R_A = R_B$ (that is, if both atoms belong to the same row of the periodic table) the bond length d is nearly constant for $N = 2,3,4$. This means that the homopolar parts of the energy gaps of BN, AlP and GaAs, corresponding to $R = 1,2$ and 3, can be obtained from those of diamond, silicon and germanium respectively. In each case nature furnishes us with a homopolar analog of the heteropolar compound. More generally, in all cases E_h can be determined from d, R_A and R_B. One finds that $E_h(d)$ varies like $d^{-2.5}$, and that E_h plays the role of Pauling's universal constant. In fact, E_h varies from 13.6 eV in diamond to 3.1 eV in grey tin, which is a difference of more than a factor of four.

The spectroscopic definition of covalent and ionic energies relies on the fact that in crystals the valence electrons are itinerant (not localized on atoms). In this case there are no Lorentz local-field corrections, and one can define a simple approximate relationship between the electronic dielectric constant ϵ_0 (AB) and the average energy gap E_g between bonding and antibonding states

$$\epsilon_0(\mathrm{AB}) \approx 1 + \left[\frac{\hbar\omega_p}{E_g(\mathrm{AB})}\right]^2 \qquad (6)$$

where $\omega_p{}^2 = 4\pi Ne^2/m$ is the valence-electron plasma frequency, with N the density of eight valence electrons per AB unit volume. One can show that the neglect of local-field corrections in equation 6 is valid so long as $\epsilon_0 \gtrsim 2$.

The average energy gap E_g includes the effects of both covalent and ionic energies. In $A^N B^{8-N}$ crystals, off-diagonal matrix elements of these terms are 90 deg out of phase (a result derivable from structure factors), so that

$$E_g{}^2 = E_h{}^2 + C^2 \qquad (7)$$

where $C = C(\mathrm{AB})$ is the average ionic energy gap. Given $E_h = E_h(d)$, one can infer $C(\mathrm{AB})$ from ϵ_0 (AB), according to equations 6 and 7. It turns out that the values of $C(\mathrm{AB})$ so derived are closely proportional to $(X_A - X_B)$ as defined by Pauling. Representative examples are shown in figure 4.

Given *both* E_h and C, one has now an obvious definition of f_i that does not encounter Pauling's dimensional difficulties. It is

$$f_i(\mathrm{AB}) = \frac{C^2(\mathrm{AB})}{E_h{}^2(\mathrm{AB}) + C^2(\mathrm{AB})} \qquad (8)$$

The definition of equation 8 also satisfies equations 6 and 7. It also has the simple geometrical interpretation shown in figure 5 in terms of an ionicity phase angle φ in the (E_h, C) plane. In terms of φ the definition in equation 8 is simply $f_i = \sin^2\varphi$.

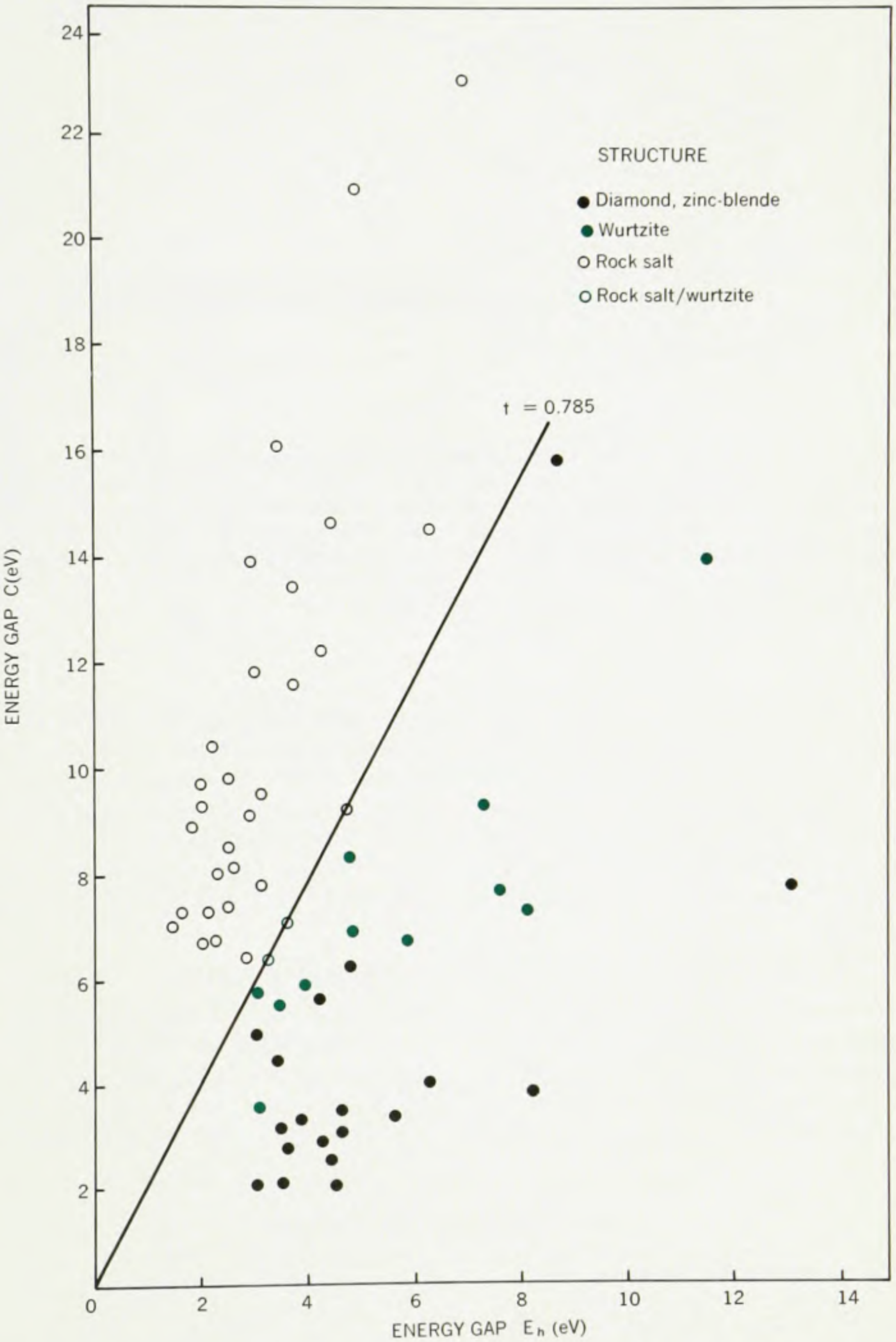
Applying the test

We have applied the statistical test (equation 1) to the two definitions (equation 3 and equation 8), with results shown in figure 6. Pauling's definition (equation 3) gives $N_0 = 8$, one below par. The dielectric definition gives $N_0 = 0$. From a statistical point of view the dielectric definition is at least twenty times more accurate than Pauling's. It follows from equation 8 and figure 5 that, when the crystal structures are plotted in figure 7 in the (E_h, C) plane, the line

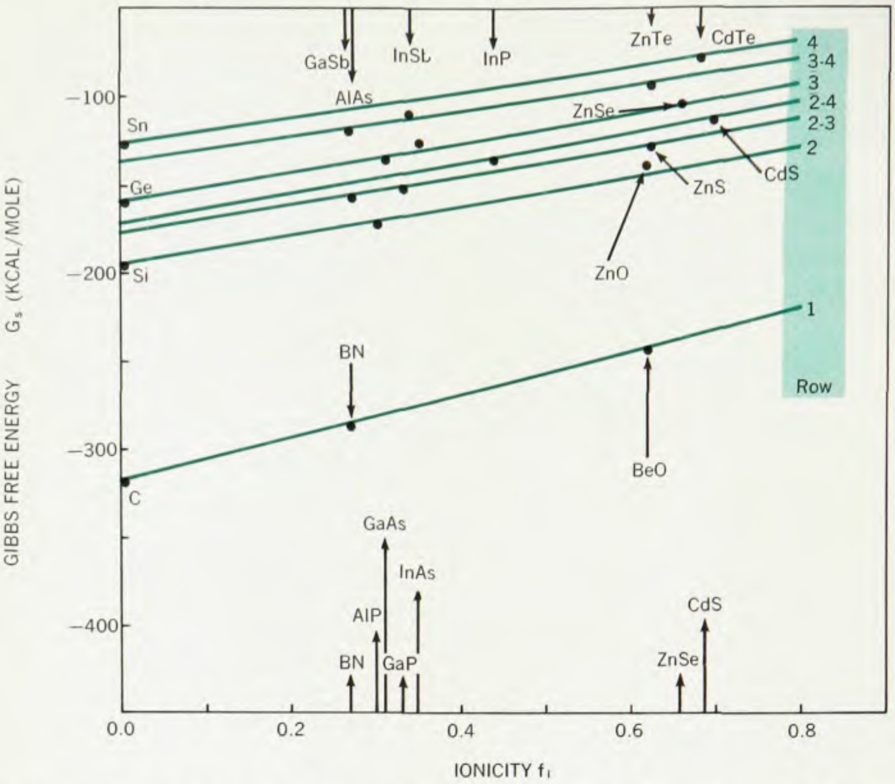
$$\varphi = \arcsin{(0.785)}^{1/2} \qquad (9)$$

will separate the first quadrant into two domains, the lower of which contains only four-fold coördinated structures, and the upper one only six-fold coördinated structures.

Some numerical examples may help to make the differences between the two definitions, equations 3 and 8, more concrete. Of particular interest are the ten borderline crystals shown in Table 1, five having four-fold coördination, and five six-fold coördination. For both scales the *average*



POPULATION DISTRIBUTION of the structures of $A^N B^{8-N}$ crystals in the (E_h, C) plane. Diamond or zinc-blende structure, with a coördination number of 4, is shown as black dots. Colored dots show wurtzite-structure crystals, also with a coördination number of 4. Black open circles show crystals with a rock-salt structure and a coördination number of 6. The two open colored circles are for rocksalt/wurtzite metastable structure and coördination numbers 6 or 4 at room temperature. Notice that the line for $f_i = 0.785$ separates the quadrant into four-fold structure and six-fold structure domains. —FIG. 7



GIBBS FREE ENERGY OF ATOMIZATION at STP, plotted against ionicity as defined by equation 8, is a test of our new scale of ionicity. Here are shown different combinations of R_A and R_B, the rows of the periodic table that contain elements A and B, as labelled in the colored panel at the right. The examples in this graph are all four-fold coördinated semiconductors. In most cases for sequences of $A^N B^{8-N}$ such that all A's are in row R_A and all B's in row R_B, we find linear relations to within the limits of experimental accuracy (about 1% on both axes). —FIG. 8

ionicity of the latter group exceeds that of the former by about 0.1. However, the scatter associated with Pauling's scale is ten or twenty times greater than that of the dielectric scale (labelled "Phillips" in the table), so that the former is simply not accurate.

We mentioned earlier that one would expect an ionicity gap $\Delta F_i = F_i^6 - F_i^4$ between the two coördination structures that are separated by a first-order phase transition. The results obtained from the dielectric scale given in Table 1 indicate that $\Delta F_i <$ 0.01; that is, within the limits of statistical accuracy, there is *no discontinuity*. Thus quantum theory provides a super-scale of greater structural significance than anything obtainable from classical thermodynamic reasoning. I found this result surprising.

A true scale of ionicity?

The simple analytic form of equation 8 together with its remarkable accuracy suggest that it may actually be a *true scale* for ionicity of the chemical bond. To test this conjecture I plotted[8] the cohesive energies ΔG_s (more accurately defined as the Gibbs free energy of atomization at STP) against f_i for combinations of R_A and R_B. The results are shown in figure 8. Clearly the energies are very nearly linear in f_i. The superiority of the dielectric approach is particularly striking for $R_A = R_B = 1$, where the covalent bond is very strong.

Table 1. Borderline Ionic Characters

FOUR-FOLD COÖRDINATION			SIX-FOLD COÖRDINATION		
Crystal	*Ionicity*		*Crystal*	*Ionicity*	
	Pauling	Phillips		Pauling	Phillips
CdTe	0.04	0.675	MgS*	0.34	0.786
CdSe	0.15	0.699	MgSe*	0.29	0.790
CuBr	0.18	0.735	MgO	0.73	0.841
CuCl	0.67	0.746	AgBr	0.18	0.850
AgI	0.04	0.770	AgCl	0.26	0.856
Average	0.22	0.72	Average	0.36	0.83

* Metastable in four-fold coördination.

From the review I have given here it is clear that theoretical solid-state physics may have reached the level of sophistication required to elucidate chemical trends throughout the periodic table. I have dealt here with only one aspect of this sophistication; I should also mention that Frank Herman has calculated the energy bands and optical spectra of more than 50 crystals, and Phil Anderson has recently studied the foundations of the Hückel theory (to which the dielectric theory bears a close formal resemblance). Vod Heine and coworkers at Cambridge have calculated pseudopotential form factors for more than 30 nontransition elements, and Marvin Cohen and coworkers at Berkeley have related pseudopotential form factors to many crystalline properties, including optical spectra and superconductivity. Perhaps Pauling was right after all, although the mathematical justification of many of his ideas will be made by physicists rather than by chemists!

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