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Dielectric Methods of Studying the Chemical Bond and the Concept of Electronegativity

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The history and contemporary theories of the polarisation of molecules and crystals are considered and a systematic survey is given of dipole moments and bond ionicities in molecular chemical compounds and also of the effective charges of atoms in crystals. An interpretation of these results is given from the standpoint of the electronegativity concept. Views concerning the effective valencies and coordination numbers of atoms in crystals are considered. Bibliography of 207 references

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I. INTRODUCTION

Polarisation, that is, the separation of charges in an electric field, was the first physical characteristic of molecules which allowed the nature of the chemical bond to be determined quantitatively, and in particular, its degree of ionicity (sometimes termed polarity, from the name of the determining parameter). It is extremely significant that the information which can be extracted from polarisation measurements is unique and constitutes the main component of such structural-chemical characteristics of bonds as dipole moments, effective charges, and valencies of the atoms.

II. POLARISATION AND THE DIPLE MOMENTS OF MOLECULES

In general, molecular polarisation can be represented as:

$$P_m = \frac{M}{\rho}\frac{\varepsilon-1}{\varepsilon+2} = \frac{4}{3}\pi N\left(\alpha + \frac{\mu^2}{3kT}\right), \qquad (1)$$

where P_m is the molecular polarisation, M the molecular mass, ρ the density of the substance, ε the dielectric permittivity, N the Avogadro number, α the polarisability of the molecule, and μ the dipole moment. Clearly, when $\mu = 0$, P_m will be independent of temperature.

A method for the experimental determination of μ follows from Eqn.(1): by measuring P_m at various T the polarisability and dipole moment can be found separately. Information about dipole moments is of independent interest and there is a considerable literature on this subject, which we will not deal with. Table 1 gives the dipole moments of the molecules of the alkali metal, silver, thallium, carbon, and phosphorus halides and also the tin and lead chalcogenides, from Lovas and Tiemann[1].

Since by definition

$$\mu = e^* r , \qquad (2)$$

where e^* is the effective charge on an atom and r the length of a chemical bond, clearly the ratio μ/r should characterise the polarity of the chemical bond (p). In addition to μ, Table 1 gives the ratio $p = \mu/4.8r$.

The second term on the right-hand side of Eqn.(1) corresponds to the orientation part of the total polarisation and is usually denoted by P_o. When a molecule is inserted into an electric field, not only its orientation, but also its deformation—extension of polar atoms in the field direction—take place. This part of the polarisation is termed atomic polarisation, P_a. The deformation of the electronic cloud of the molecule is denoted by P_e. Consequently, the total polarisation consists of P_o, P_a, and P_e. In solids, where $P_o \cong 0$, we obtain $P_m = P_a + P_e$. Obviously, for non-polar substances $P_a = 0$ and $P_m = P_e$. Hence a comparison of the experimental values of P_a and P_e or of P_m and P_e can give qualitative information about the bond polarity.

Table 1. Dipole moments and bond polarities.

Element	μ, D	p	μ, D	p	μ, D	p	μ, D	p
	F		Cl		Br		I	
H	1.91	0.43	1.08	0.18	0.79	0.12	0.38	0.05
Li	6.33	0.84	7.13	0.73	7.27	0.70	7.43	0.65
Na	8.155	0.88	9.00	0.79	9.12	0.79	9.24	0.71
K	8.59	0.82	10.27	0.80	10.63	0.78	10.82	0.74
Rb	8.55	0.78	10.51	0.78	10.86	0.77	11.48	0.75
Cs	7.88	0.70	10.39	0.74	10.82	0.73	11.69	0.73
Ag	6.22	0.65	5.70	0.52	—	—	—	—
Tl	4.23	0.42	4.54	0.38	4.49	0.36	4.61	0.34
C	1.41	0.22	1.46	0.17	1.38	0.13	1.19	0.12
P	0.77	0.10	0.81	0.08	0.36	0.03	0	0
	O		S		Se		Te	
Sn	4.32	0.49	3.18	0.30	2.82	0.25	2.19	0.18
Pb	4.64	0.50	3.59	0.33	3.28	0.28	2.73	0.22

Despite the qualitative validity of such comparisons the precise relation between the polarisation and the electronic structure of a substance has been found only within the framework of a spectroscopic approach[2,3], which has established a connection between the polarisability of the vibrations of the atom which are taking place and its effective charge (e^*). Some investigators[4-6] used this approach to determine the charges on the atoms in halides of Group IV elements.

Another direction of the work to find bond polarities by a spectroscopic method is based on the measurement of the intensities of infrared absorption bands of molecules to determine e^* as a function of the derivative of the dipole moment with respect to bond length. The history of the problem and the results of the determination of effective charges in Group IV element hydrides have already been given[7].

Hence the spectroscopic values of the atomic charges are also approximate owing to the neglect of a series of factors, namely, anharmonicity and the changes in the orbital overlaps during vibrations, but where molecules are concerned—and consequently the inductive influence of substituents—mainly due to the complexity of the "dipole moment" concept itself.

Without dwelling on the history of the development of theoretical opinions on the nature of dipole moment, we will refer only to Brumer and Karplus's work[8], in which a quantum-mechanical basis was given for the well-known Rittner formula, according to which

$$\mu \simeq er\left(1 - \frac{\alpha_A + \alpha_B}{r^3} + \frac{4\alpha_A\alpha_B}{r^6}\right), \qquad (3)$$

where α_A and α_B are the polarisabilities of ions A and B.

The last theoretical investigation of the dipole moments of ionic molecules is that of Matcha and King[9], who took into account not only effective charges and the polarisability of atoms, but also the moments of the orbital overlaps and the repulsion of the electron clouds. The experimental values of e^* determined in that work[9] are given in Table 2; extrapolated values of the charges on the atoms are also given there (in parentheses).

Table 2. Charges of the atoms in alkali halide molecules.

A	B			
	F	Cl	Br	I
Li	0.87	0.82	(0.79)	(0.76)
Na	0.89	0.86	0.84	0.81
K	0.93	0.91	(0.89)	(0.86)
Rb	0.94	0.92	(0.90)	(0.87)
Cs	0.99	0.96	(0.94)	(0.91)

The relation between the bond polarity (p.1202) and e^* [9] is expressed by the formula:

$$e^* \simeq p\left(1 - \frac{\alpha_A + \alpha_B}{r^3}\right)^{-1}. \qquad (4)$$

Hence it is clear that the reduced value of p in CsF in comparison with other alkali metal fluorides (cf. Table 1) is due to the greater polarisability of the caesium ion.

As for the dipole moments of covalent bonds, Mulliken[10] found by LCAO MO theory that the dipole moment consists of three terms: the ionic moment, $\pm e^* r$; a covalent term, $\mp 4eabs$ where a and b are the weighting factors of the atomic wave functions, and S is the overlap integral; and the moment of the isolated electron pair, $\pm\mu_S$.

The next broad step on the theory of dipole moments was taken by Coulson[11], who, by analysing the charge distribution in the C–H bond by the MO method, concluded that for hybrid orbitals in addition to the three Mulliken terms allowance must be made for the hybridisation moment.

Hence bond ionicities can only be calculated from measured dipole moments if the remaining components of the bond moment are determined empirically or theoretically. Therefore subsequently in addition to the accumulation of new experimental results the main attention was directed at these particular problems[12–18].

III. BOND IONICITY AND ELECTRONEGATIVITY OF ATOMS IN MOLECULES

Since in general the charges on atoms cannot be determined in the simplest manner—by Eqn.(2)—Pauling proposed that the variation of bond ionicity† with the electrochemical properties of its component atoms be found and then the charges determined directly from these characteristics of the atoms.

The concept Pauling used as such a property was the electronegativity of an atom, that is, its ability to attract valence electrons. The history of this[19–22] will not be discussed here other than to point out that electronegativity can be determined:

(1) from thermodynamic data by the equation:

$$X_A - X_B = E(A-B) - \frac{1}{2}[E(A-A) + E(B-B)], \qquad (5)$$

where X_A and X_B are the electronegativities of the atoms A and B, and E(A–A), E(A–B), E(B–B) are the A–A, A–B, and B–B bond energies.

(2) from ionisation potentials and electron affinities:

$$X = \frac{1}{2}(I + A), \qquad (6)$$

where I is the first ionisation potential and A the affinity for one electron of the atom in the valence state;

(3) from the covalent radii (r) and effective nuclear charge (z^*):

$$X = az^*/r^b + c; \qquad (7)$$

(4) from the spectroscopic characteristics of the bonds between the atoms:

$$k = a(X_A X_B/r^2)^b + c \text{ or } \Delta X_{AB} = m\nu_{AB} + n, \qquad (8)$$

where k is the force constant of the bond; ν the characteristic frequency of the vibrations of the bond A–B; and a, b, c, m, and n are constants.

The literature on the determination and use of atom electronegativities is so great that it cannot be cited completely in a journal paper. Therefore we will quote only the principal, mainly review, papers plus investigations carried out after 1968.

Thermochemical determinations of electronegativity based on Pauling's equation, Eqn.(5), have been carried out[23–26]; the averaged results of these studies are given in the first sub-lines of Table 3.

Electronegativities have been determined with Mulliken's equation, Eqn.(6).[27–39] The ionisation potentials of atoms in the valence state cannot be determined experimentally when the valence state does not coincide with the ground state, since then a knowledge of the promotion energies of the electrons is required. Consequently most studies in this direction are quantum-mechanical. The ideas of the electronegativity of an atom depending on the orbital type of its bonds ("the orbital electronegativities of atoms") arose in this particular region.

† Bond ionicity is essentially a synonym for the effective charge of an atom; the ionicity is usually expressed in percentages of the formal charge, the effective charge in fractions of the electronic charge.

Table 3. Electronegativities of the atoms in molecules, determined by various methods.

Period	1A	2A	3A	4A	5A	6A	7A	8A	1B	2B	3B	4B	5B	6B	7B
II	Li 1.0 0.9_5 0.9 0.9_5	Be 1.5 1.4 1.4_5 1.4_5									B 2.0 1.9 1.9 1.9	C 2.6 2.4 2.4_5 2.5_5	N 3.0 2.8 3.0 3.0	O 3.5 3.3_5 3.4_5 3.4_5	F 4.0 3.9_5 4.0 3.9_5
III	Na 0.9 0.9 0.9 0.9	Mg 1.3 1.2 1.2 1.2									Al 1.6 1.6 1.4 1.5	Si 1.8 2.0 1.7 1.8	P 2.1 2.2 2.0_5 2.1	S 2.6 2.5 2.5 2.5	Cl 3.1 2.9 2.9 3.0
IV	K 0.8 0.8_5 0.8 0.8	Ca 1.0 1.1 1.0 1.0	Sc 1.3 1.3 1.3 —	Ti 1.5 1.5 1.5 2.0	V (III) 1.7 1.5 1.7 2.0	Cr (III) 1.9 1.6 1.7 2.0	Mn (III) 1.7 1.7 1.8 2.2	Fe (III) 1.9 1.7 1.9 2.3	Co (III) 2.0 1.8 2.0 1.8	Ni (III) 2.0 1.9 2.1 2.0	Cu 1.9 1.6 1.8 2.2	Zn 1.6 1.5_5 1.8 1.4	Ga 1.7 1.7 1.9 1.4	Ge 1.9 2.1_5 2.0_5 1.7	As 2.0 2.2 2.2 2.0	Se 2.5 2.4 2.5 2.4	Br 2.9 2.7 2.7_5 2.7_5
V	Rb 0.8 0.8 0.8 0.8	Sr 1.0 1.0 1.0 1.0	Y 1.2 1.2 1.2 —	Zr 1.4 1.4 1.4_5 1.6	Nb (III) 1.6 1.3 1.6_5 —	Mo (IV) 2.0 1.7 1.7 1.9	Tc (IV) 1.9 1.6 1.8 2.2	Ru 2.2 1.8 2.0 2.0	Rh 2.2 1.9_5 2.1 2.3	Pd 2.2 2.0_5 2.1 —	Ag 1.9 1.4 1.7 1.9	Cd 1.7 1.4 1.7 1.4	In 1.8 1.6 1.8 1.4	Sn (II) 1.8 2.0 1.9 1.7	Sb (III) 1.9 1.9 2.0 1.8	Te 2.1 2.2 2.2 2.1	I 2.6 2.6 2.4 2.4_5
VI	Cs 0.7_5 0.7 0.8 0.7_5	Ba 0.9 0.9_5 1.0 0.9	La 1.1 1.2 1.2 —	Hf 1.3 1.4 1.6 1.5	Ta (III) 1.5 1.4 1.8 —	W (IV) 2.0 1.7 1.9 1.7	Re (IV) 1.9 1.6 2.0 2.0	Os 2.2 1.9_5 2.1 2.2	Ir 2.2 2.1 2.2 2.2	Pt 2.2 2.1_5 2.2 2.3	Au 2.4 1.6 2.0 3.1	Hg 1.9 1.5 1.9 1.5	Tl (III) 2.0 1.6 1.9 1.3	Pb (II) 1.9 1.9 1.9 1.5	Bi (III) 1.9 1.8 2.0 1.8	Po 2.0 1.9_5 2.1 —	At 2.2 2.4_5 2.3 —

Table 4. System of the electronegativities of the atoms in molecules*.

Period	1A	2A	3A	4A	5A	6A	7A	8A	1B	2B	3B	4B	5B	6B	7B
II	Li 0.9_5	Be 1.5									B 1.9	C 2.5	N 3.0	O 3.5_5	F 4.0
III	Na 0.9	Mg 1.2									Al 1.5	Si 1.9	P 2.1	S 2.5	Cl 3.0
IV	K 0.8	Ca 1.0	Sc 1.3	Ti 1.6	V (II) 1.5 (III) 1.7 (V) 2.0	Cr (II) 1.6 (III) 1.8 (VI) 2.2	Mn (II) 1.5 (III) 1.8 (IV) 2.0 (VII) 2.3	Fe Co Ni (II) 1.8 1.8 1.9 (III) 1.9 2.0 2.0 (IV) — 3.1 3.4	Cu (I) 1.8 (II) 2.1	Zn 1.6	Ga 1.7	Ge 2.0	As 2.0	Se 2.4	Br 2.8
V	Rb 0.8	Sr 1.0	Y 1.2_5	Zr 1.5	Nb (III) 1.6 (V) 1.9	Mo (IV) 1.8 (VI) 2.2	Tc (IV) 1.9	Ru Rh Pd (II) 2.0 2.0 2.1 (III) 2.1 2.1 — (IV) 2.2 2.2 2.3	Ag 1.9	Cd 1.7	In 1.8	Sn (II) 1.8 (IV) 2.0	Sb (III) 1.9 (V) 2.2	Te 2.1	I 2.5
VI	Cs 0.7_5	Ba 0.9	La 1.2	Hf 1.4	Ta (III) 1.5 (V) 1.8	W (IV) 1.8 (VI) 2.1	Re (IV) 1.9	Os Ir Pt (II) 2.0 2.1 2.2 (III) 2.1 2.2 — (IV) 2.3 2.3 2.4	Au (I) 2.0 (III) 2.4	Hg 1.8	Tl (I) 1.4 (III) 1.9	Pb (II) 1.9 (IV) 2.1	Bi (III) 1.9 (V) 2.2	Po 2.0	At 2.2
VII	Fr 0.7	Ra 0.9	Ac 1.1												
Actinides				Th (IV) 1.3	Pa (IV) 1.3 (V) 1.5	U (IV) 1.4 (V) 1.6 (VI) 1.8									

*$X_M = 2.1$.

Many investigators regard the determination of electronegativities from ionisation potentials as the most substantiated physically. Consequently the difference in the dimensionalities of the thermochemical and ionisation electronegativities was thought[40] to be a defect of the electronegativity concept. However, Martynov and Batsanov[37] have shown that the use of not the first ionisation potential but the mean value of the potential for all the outer electrons ($\bar{I}$) leads to an equation of the type:

$$X = a(\bar{I})^{1/2} + b \quad , \qquad (9)$$

where X has the same dimensionality as the thermochemical electronegativity of the atoms. The ionisation electronegativities are given in the second sub-lines of Table 3.

Calculations of the electronegativities of the atoms from their radii and the effective charges of the atomic nuclei by equations of the type of Eqn.(7) also have a history of many years and are continuing vigorously to the present time[41-50]. Averaged electronegativities from these studies are given in the third sub-lines of Table 3.

Spectroscopic determinations of electronegativities are based either on the use of the force constants of the bonds[51,52] or the wavenumbers of the vibrations in the

ultra-violet[53–59] infrared[60–64], or radio-wave[65–67] regions of the spectrum, or chemical shifts in the Mössbauer spectra[68,69]. The averaged atomic electronegativities from optical spectroscopic results are given in the fourth sub-lines of Table 3.

As Table 3 shows, the results of the electronegativity calculations by various methods agree very well, which allows a universal system of electronegativities of the elements to be constructed. Table 4 gives such a system for the atoms in various oxidation states.

Pauling deduced the following relation from a comparison of the dipole moments and electronegativities of the atoms[23]:

$$i = 1 - e^{-a\Delta X^2}, \qquad (10)$$

where a is a constant, which, determined after refinement of the dipole moment of HF, equals 0.18. Analysis of Eqn.(10) and confirmation of its validity by independent methods are considered in a book[19].

Nethercot[70] recently took the next step in the direction of the formal development of Eqn.(10). He suggested that i should be expressed as a function not of ΔX but of the normalised difference in the electronegativities of the atoms:

$$i = 1 - e^{-a\Delta \bar{X}^2}, \qquad (11)$$

where

$$\Delta \bar{X} = \Delta X/(X_A X_B)^{1/2}.$$

The successful solution of the problem of finding i from ΔX (using the dipole moments of the HHal molecules) allowed the reverse problem to be solved also—the finding of μ (for example, for organic molecules) from the electronegativity and i.[71]

IV. POLARISATION OF CRYSTALS: BORN AND SZIGETI'S THEORETICAL APPROACH

The development of the theory of polarisation of ionic crystals began with the well-known equation of Born and Göppert-Meyer, in which the dielectric permittivity is linked with the natural frequency of the transverse lattice vibrations:

$$\varepsilon = n^2 + \frac{4\pi(ze)^2}{\omega_i^2 \bar{M} V}. \qquad (12)$$

Here ω_i is the frequency of the transverse lattice vibrations, V the volume associated with one particle, $\bar{M}$ the reduced mass of the vibrating particle, n the refractive index, and z the valency of the ion.

Comparison of the experimentally measured and theoretical (calculated from the Born formula) values of ε showed that usually the calculated ε were less than the experimental values. The reason for the discrepancy between theory and experiment is in the assumption, made in the theory, that the interaction of the ions is coulombic and that P_a and P_e are additive. Actually, the electron clouds of the ions in the crystals are deformed and are overlapped during the vibrations of the lattice, as a result of which the atomic and electronic components of the polarisation are no longer independent additive quantities.

Szigeti[72] showed that the deformation of the electron cloud of the ions due to the transverse vibrations of the lattice increases the atomic polarisation. On taking into account also that the field strength E in the dielectric is less than the external field due to the polarisation of the specimen, Szigeti obtained the following equation:

$$\varepsilon = n^2 + \frac{4\pi(ze)^2}{\omega_i^2 \bar{M} V}\left(\frac{n^2+2}{3}\right)^2. \qquad (13)$$

The Szigeti equation differs from the Born formula by the factor $[(n^2+2)/3]^2$, which takes into account the contribution from electronic polarisation to atomic polarisation. This term plays a greater part the higher the refractive index, that is, the greater the covalency of the bond; it is in just these circumstances that Born's assumption that isolated ions are not deformed is least valid.

Comparison of the result of calculations by Eqn.(13) with experiment showed that the calculated values of ε are always greater than those measured experimentally. This led Szigeti to the idea of changing the formal charge of the ion z to some quantity s which characterises the departure of the actual charge e^* from the theoretical value. It is easy to see that in the physical sense the parameter s is the effective charge of the atom: $s = e^*$. On taking into account that

$$\omega_t = 2\pi\nu_t,$$

where ν is the experimentally determinable linear transverse vibration frequency of the lattice, Szigeti deduced that

$$e^* = \frac{3\nu_t c}{ze\,(n^2+2)}[\pi(\varepsilon - n^2)\bar{M}V]^{1/2}, \qquad (14)$$

where e^* is the effective charge of the atom, which reflects the bond ionicity in the crystal.

Hence on the basis of characteristics of the crystal such as its molecular mass, volume, the frequency of the vibrations of the atoms the dielectric permittivity, and the refractive index, the Szigeti equation allows the departure of the bond character from the purely ionic state to be determined.

Table 5. Effective charges of the atoms in crystals of type AB (according to Szigeti).

AB	e^*/z	Reference	AB	e^*/z	Reference	AB	e^*/z	Reference
LiH	0.53	74	CuO	0.54	79	PbO	0.58	93
LiF	0.81	75	BeO	0.55	80	PbS	0.36	83
LiCl	0.78	75	MgO	0.59	79	PbSe	0.35	79
LiBr	0.74	75	MgS	(0.62) **	79	PbTe	0.28	79
LiI	0.54	75	CaO	0.61	81	MnO	0.55	79
NaF	0.83	75	CaS	0.52	79	α-MnS	0.44	94
NaCl	0.77	75	SrO	0.61	81	γ-MnS	0.35	94
NaBr	0.75	75	SrS	0.53	79	MnSe	0.42	94
NaI	0.74	75	BaO	0.74	81	MnTe	0.33	94
KF	0.92	75	BaS	0.55	79	FeO	0.46	79
KCl	0.81	75	ZnO	0.60	82	CoO	0.44	79
KBr	0.77	75	ZnS	0.44	82	NiO	0.41	79
KI	0.75	75	ZnSe	0.40	82	BN	0.30	95
RbF *	0.97	75	ZnTe	0.39	82	BP	0.25	96
RbCl	0.84	75	CdO	0.59	83	AlN	0.41	83
RbBr	0.80	75	CdS	0.45	82	AlP	0.26	83
RbI	0.77	75	CdSe	0.42	82	AlAs	0.21	83
CsF *	0.96	75	CdTe	0.38	82	AlSb	0.16	83
CsCl	0.85	75	HgO	0.57	79	GaN	0.41	83
CsBr	0.82	75	α-HgS	0.20	84	GaP	0.19	83
CsI	0.78	75	β-HgS	0.28	85	GaAs	0.17	83
CuCl	0.98	76	HgSe	0.27	86	GaSb	0.13	83
CuBr	0.96	76	HgTe	0.26	87	InP	0.22	83
CuI	0.91	76	EuO	0.67	88	InAs	0.18	83
AgF	0.89	77	EuS	0.54	89	InSb	0.14	83
AgCl	0.71	77	EuTe	0.50	90	SiC	0.22	83
AgBr	0.67	77	SnS	0.33	79			
AgI	0.61	77	SnSe	0.27	91, 92			
TlCl	0.88	77	SnTe	0.26	83			
TlBr	0.84	77						
TlI	0.83	77						
HgCl	0.70	78						

* Charges of the atoms recalculated according to the X-ray densities[97].

** Estimated value.

The Szigeti equation was used initially to calculate the effective charges of the atoms for only simple cubic crystals, but as time elapsed more and more complex crystalline compounds were studied, both isotropic and anisotropic. The

development of the Szigeti method is linked with the perfection of the measuring techniques and with the refinement of the method of calculating the optical characteristics of anisotropic crystals.

Most anisotropic crystals are characterised by infrared spectra so complex that the choice of the frequencies of the transverse and longitudinal vibrations—ν_t and ν_l—for calculation of charges is a special problem. This has been considered by Loudon[73] for uniaxial crystals as example. It was found that usually some of the bands in the infrared reflection spectra of the uniaxial crystals hardly shift on going from the orientation of the electric field parallel to the c axis towards a perpendicular orientation, that is, $\nu_\parallel \cong \nu_\perp$. If the inequality

$$|\nu_\parallel - \nu_\perp|_{l \text{ or } t} \ll (\nu_l - \nu_t)_{\parallel \text{ or } \perp}, \qquad (15)$$

holds in this, then these bands correspond to isotropic oscillators, since the internal field is then analogous to the field of the cubic crystals. Here it has been shown[73], that the strength of the isotropic field is a maximum for the highest frequency vibrations which satisfy inequality (15).

Tables 5 and 6 give the results of experimental investigations on crystalline compounds by the Szigeti method. The literature reference in Tables 5 and 6 are usually for the latest papers on these compounds, which have been studied repeatedly, or for those papers in which there are the most accurate physical characteristics of the crystals, although the calculations of effective charges were not carried out.

Table 6. Bond ionicities in crystals of type A_nB_m (according to Szigeti).

Substance A_nB_m	e^*/z	Reference	A_nB_m	e^*/z	Reference	A_nB_m	e^*/z	Reference
MgF_2	0.76	98,99	CoF_2	0.74	99	$HfSe_2$	0.45	116
CaF_2	0.84	100,101	$CoCl_2$	0.41	107	MoS_2	0.06	117
SrF_2	0.85	102	$CoBr_2$	0.40	107	$MoSe_2$	0.04	118
$SrCl_2$	0.76	103	NiF_2	0.68	99]	ThO_2	0.60	119
BaF_2	0.87	102	$NiCl_2$	0.40	107	UO_2	0.58	119
ZnF_2	0.76	98,99	$NiBr_2$	0.35	107	CeO_2	0.48	120
CdF_2	0.83	104	NdOF *	0.76	108	ScF_3	0.76	121
$CdCl_2$	0.72	104	Na_2S	0.58	109	YF_3	0.76	108, 121
$CdBr_2$	0.69	104	Cu_2O	0.29	110	LaF_3	0.74	108
CdI_2	0.67	104	TiO_2	0.60	111	AlF_3	0.60	121
HgI_2	0.38	105	TiS_2	0.39	112	GaF_3	0.60	121
EuF_2	0.84	106	$TiSe_2$	0.18	112	InF_3	0.61	121
PbF_2	0.95	104	SiO_2	0.60	111	Y_2O_3	0.62	120
$PbCl_2$	0.90	104	GeO_2	0.54	111	Y_2S_3	0.40	122
PbI_2	0.75	104	GeS_2	0.18	113,114	La_2O_3	0.62	108
MnF_2	0.81	99,101	$GeSe_2$	0.17	92]	La_2S_3	0.40	122
$MnCl_2$	0.50	107	SnO_2	0.57	111	Al_2O_3	0.59	111
$MnBr_2$	0.50	107	SnS_2	0.32	115	Cr_2O_3	0.46	111
FeF_2	0.68	98]	$SnSe_2$	0.25	115	As_2S_3	0.20	123
$FeCl_2$	0.42	107	ZrS_2	0.44	116	As_2Se_3	0.14	123
$FeBr_2$	0.41	107	HfS_2	0.50	116			

* Since the atoms O and F have similar sizes and masses, these compounds are close to type AB_2.

Table 5 allows a series of conclusions to be drawn. The values of e^* increase with the difference in the electronegativities of the atoms A and B, and also with the coordination numbers of the atoms in the crystal structures. Thus going from α- to β-HgS is accompanied by an increase in the number of nearest neighbours from 2 to 4, and for α- and γ-MnS the coordination numbers are changed from 6 to 4. The bond ionicity increases with the coordination of the atoms, which is in complete agreement with Pauling's postulate[23]. It should also be noted that the difference in the bond ionicities of analogous compounds of the elements of the A and B subgroups was significantly less than could be expected from a comparison of the electronegativities of atoms in molecules (Table 4).

Table 6 gives the results of studies on crystalline compounds of type A_nB_m by the Szigeti method. When the values of e^* in the papers cited were calculated by the Born equation they were recalculated by Eqn.(14). In the treatment of the published data for MnF_2, Cu_2O, GeS_2, and $GeSe_2$ the choice of the lattice vibration frequencies was made with allowance for Eqn.(15).

The data in Table 6 agree with the changes in the electronegativities of the atoms but there are significant discrepancies for several compounds. Thus the bond ionicities in the Pb halides are very high, which Axe and coworkers[124] explained by the increased valency of lead in these compounds; the bond ionicities in the molybdenum chalcogenides were unexpectedly low, which Lucovsky and coworkers[116] explained by the formation in this instance of the radicals S_2 and Se_2, the oxidising abilities of which are considerably lower than those of S and Se atoms.

The low bond ionicity for copper(I) oxide compared with copper(II) oxide (and with the calculation by the electronegativity method) must show a decrease in the effective valency of copper in Cu_2O. We will return to the problem of effective valencies; here we will only note that according to X-ray diffraction studies[125], there is a Cu–Cu bond in Cu_2O.

Not only binary compounds, but also double salts and complexes have been studied by the Szigeti method. In every instance it was found that the ionicity of the bonds in the inner sphere of complexes is higher than that in the corresponding binary compounds.

Analysis of the infrared spectra of binary oxides and complexes allows the Szigeti equation to be used for determining the effective charges not only on ionic complexes but also in the inner sphere of these complexes. Table 7 gives the results of investigations of the effective charges of the atoms in complexes[111,126,127].

Table 7. Effective charges of the atoms in oxygen compounds.

M_nAO_m	e^*/z (M)	e^*/z (A)	e^*/z (O)	M_nAO_m	e^*/z (M)	e^*/z (A)	e^*/z (O)
$NaNO_3$	0.92	0.04	0.18	$SrTiO_3$	0.80	0.71	0.75
$RbClO_3$	0.90	0.16	0.28	$BaTiO_3$	0.82	0.64	0.70
$MgCO_3$	0.67	0.11	0.26	$PbTiO_3$	0.85	0.53	0.62
$NdAlO_3$	0.84	0.40	0.62	$LiNbO_3$	0.77	0.62	0.64
Be_2SiO_4	0.65	0.46	0.55	$LiTaO_3$	0.79	0.67	0.69
Mg_2SiO_4	0.73	0.42	0.58	$CaMoO_4$	0.80	0.42	0.52
$ZrSiO_4$	0.83	0.38	0.60	$CaWO_4$	0.82	0.47	0.56

Comparison of the results in Tables 5–7 shows that in compounds of the M_nEO_m type the ionicity of the M–O bond is greater, and that of the E–O bond less, than in the corresponding binary oxides of M and E. Such a distinctive compensation dependence in the ratio of various properties of complexes is constantly encountered.[128] It has been shown by the Szigeti method that there is an analogous dependence for solid solutions of binary compounds, for example, in mixed alkali halides[129].

As the KCl concentration in KCl–KBr solid solution is reduced the frequency of the vibrations and the crystal cell volume will vary monotonically from the values characteristic of KCl to those characteristic of pure KBr; the reduced

mass M also changes analogously. In addition, a peculiarity of the Szigeti equation is that the relation

$$\nu_t \sqrt{\bar{M}V} = \text{const} \quad (16)$$

is valid. This follows from the theory of a harmonic oscillator and the calculation of a force constant according to Coulomb's law. Therefore changes in the reduced mass (or molar volume) are compensated by a change in the vibration frequency, that is, for low concentrations of KCl in KCl–KBr solid solution the values of ν_t, $\bar{M}$, and V for pure KBr can be inserted into the Szigeti equation.

On considering the characteristics of an individual KCl particle in a continuous matrix of KBr, it must be assumed that the value of ε for such a solid solution will be the same as for pure KBr, since the dielectric permittivity in its physical essence relates to the medium in which this particle is located. As for the refractive index, that depends on the change in the volume of the KCl particle in the solid solution compared with the free state.

Without dwelling on the details of the calculation of the optical dielectric constants (cf. Batsanov[129]) we will pass to a statement of the results of applying the Szegeti method to the determination of the effective charges of atoms in solid solutions. Table 8 gives the bond ionicities for infinitely dilute solid solutions; in real materials there will be an intermediate situation.

Table 8. Effective charges of the atoms in pure and mixed crystals [solid solutions] MHal.

M	Initial substance MCl	Solid solution MCl–MBr		Initial substance MBr
Li	0.74	0.83	0.59	0.71
Na	0.76	0.85	0.60	0.72
K	0.80	0.88	0.67	0.77
Rb	0.85	0.89	0.72	0.80
Cs	0.86	0.92	0.72	0.81
Hal	KHal	KHal–RbHal		RbHal
F	0.93	0.90	1.00	0.95
Cl	0.80	0.76	0.92	0.85
Br	0.77	0.72	0.88	0.80
I	0.74	0.69	0.86	0.78

As Table 8 shows, the difference in the bond ionicities of the components of the solid solution is increased in the formation of a mixed crystal: the bond in the more ionic crystal becomes even more ionic, that in the less ionic becomes more covalent. The oppositely directed changes in the character of the chemical bonds of the components of the solution lead to the mutual compensation of a large part of these changes, but in all examples the integral effect is never zero; here solid solutions differ from mechanical mixtures.

It is extremely important that the opposing changes in the charges of the atoms entering into the composition of the components of the solid solution lead to the spatial approach of the atoms, which is responsible for the possible formation of a stable solution. In addition, the compensation nature of the variation of the effective charges and radii of the atoms in the solid solution leads also to compensation of the energies of the various chemical bonds, which appears thermochemically in the low enthalpies of formation of solid solutions (which, incidentally, are not equal to the simple difference of the standard bond energies of the atoms participating in the formation of the solid solution).

It is extremely tempting to study the change in the nature of the chemical bond in crystals as the thermodynamic conditions are varied, since all the components of the Szigeti equation can be determined experimentally. However, complete certainty has not been acheived even in the sign of the change in the charge on an atom as the volume of the crystal is varied. In fact, an increase in the volume of a crystal during heating should lead to a decrease in the overlap of the atomic orbitals (and consequently to an increase in the charges on the atoms), but since this increase in volume takes place due to the increase in the amplitude of the vibrations of the atoms, there should be an increase in the overlap of the electron orbitals. Hence the total change in the character of the chemical bond during the heating of the crystal should be small and, generally speaking, can be of either sign[100,130–132].

V. EFFECTIVE CHARGES AND ELECTRONEGATIVITIES OF ATOMS IN CRYSTALS

The problem of the determination of the effective charges of atoms in a molecule or in a crystal reduces to the separation of that fraction of the space in the crystal or molecule in which the calculation or measurement of the electron density of the atoms is carried out. The minima on the curves or surfaces of electron density distribution can serve as a criterion of the division of the space into atomic regions[133–135]. A comparison of the effective charges, that is, of the difference in the formal and real numbers of electrons in the region of a given atom, determined by X-ray diffraction, with the independent determination of e^* gives good agreement[21,135].

Mulliken and coworkers[136–138] developed a quantum-chemical approach to the determination of the electron density of a chemical bond; calculation by the Hartree-Fock method of the electron densities of isolated atoms and of the appropriate compounds including these atoms in their composition allows the fine peculiarities of the chemical bond to be found by comparison. Essentially, the change in the electron density distribution in the formation of covalent molecules does not exceed 10% in comparison with the isolated atoms[139], and the charge transfer (from the metal to the non-metal atom) in polar molecules correlates with the difference in the electronegativities of these atoms[140].

The problem of the theoretical calculation of the effective charges of atoms in crystals has been considered in detail in many monographs on quantum chemistry and even in simple listing of these studies would take up much space. We are therefore limited to references to the main reviews in this field, in which either original approaches are reported or summaries are given of appropriate investigations, mainly from published results. First of all there are the classical books of Pauling[23], Coulson[141], and Slater[142], but there are others[41,135,143–148].

The most important result of the numerous theoretical investigations is that despite all the stipulations and limitations the concept of "effective charge of an atom in a crystal" plays an important part in structural chemistry and allows not only many physicochemical properties of crystals to be explained but also new properties to be predicted.

In this review we will consider only those studies in which the problem of the effective charges of atoms in crystals was studied from the viewpoint of dielectric methods and the concept of electronegativity, based on this approach.

The first quantitative estimate of the charges of the atoms in crystals from results for corresponding molecules was proposed by Pauling[23]. According to him, the covalency of the

bond in the crystals will be the same fraction of the covalency in the corresponding molecules as the valency of the atoms (z) is of the coordination number (N_C):

$$i = 1 - \frac{z}{N_c} e^{-a\Delta X^2} \quad . \qquad (17)$$

This rule was confirmed by an analysis of the interatomic distances in molecules and crystals, by comparison of the bond ionicities in molecules and crystals, in the X-ray spectroscopic and photoelectronic study of the chemical bond in crystalline compounds.

As he showed himself, Pauling's rule is valid, however, only for compounds of cations of the noble gas type, since the atoms of the B subgroups can form a larger number of bonds than their valency. Additional bonds in crystalline compounds are formed by the free orbitals of the metal atoms and the unpaired electrons of the non-metal atoms. In addition, the change in N_e on going from the isolated molecules to the crystalline state is accompanied by a change in the polarisation interaction of the ions; for crystals of the alkali halides this change is responsible, for example, for 50–80% of the total e^*.[149]

Therefore for calculating the total electron density on the atoms in crystals it was proposed to take into account not only the coulombic but also the ion-dipole interaction of atoms on the basis of the ionisation potentials and the electron affinity for the valence state[19,150]. Comparison of degrees of bond ionicity thus calculated with the experimental values shows satisfactory agreement[150].

Sanderson[151,152] proposed an original method for determining bond ionicities in molecules. He suggested that the electronegativities of the atoms, or, more precisely, quantities proportional to them, the "stability ratios" S are given by:

$$S = N/qr^3 \qquad (18)$$

where N is the atomic number of the element, r the covalent radius, and q a constant, will be equalised in the formation of molecules. Hence the relation of the stabilities of the atom in the molecule AB is

$$S_{AB} = (S_A S_B)^{1/2} \quad . \qquad (19)$$

Knowing the set of covalent and ionic S, the degree of ionicity of a bond can be calculated by the equation:

$$i = (S_{AB} - S_A)/(S_{A+} - S_A) \quad . \qquad (20)$$

Comparison of the degrees of ionicity calculated by the Sanderson and Pauling methods shows a statistical mean deviation of ~10%.

The Sanderson method was developed for the calculation of the bond ionicities of molecular compounds of complicated composition[41,153,154]. The quantum-chemical aspect of the Sanderson method was developed by many investigators and these investigations were surveyed by Jolly and Perry[155].

A variant of the Sanderson method suitable for calculating bond ionicities in coordination crystals was proposed recently[156]. This consists essentially in the calculation of S of the atoms A and B in crystals AB by the equation:

$$\bar{S}_A = (S_A \cdot S_B^{\alpha})^{1/(\alpha+1)} \text{ or } \bar{S}_B = (S_B S_A^{\alpha})^{1/(\alpha+1)} \quad , \qquad (21)$$

where α is the reduced Madelung constant.

Then $\bar{S}_A$ and $\bar{S}_B$ are compared with the values of S of the same atoms in the purely ionic and purely covalent bonds in the crystalline state with the aid of an equation of type (20), since the effective charges for cation A and for anion B in the crystal AB should equal one another.

Table 9 gives, as an example, the results of calculating the effective charges of the atoms in alkali halides (cf. Batsanov[156]). The agreement of these results with the independently determined effective charges of the atoms is also rather good, which indicates the correctness of the method of calculation and the objective significance of the effective charges themselves.

Table 9. Effective charges of the atoms in crystals calculated by the method of equalising S.

AB	e^*_A	e^*_B	AB	e^*_A	e^*_B
NaF	0.92	0.92	RbF	0.98	0.95
NaCl	0.80	0.82	RbCl	0.85	0.85
NaBr	0.76	0.79	RbBr	0.81	0.82
NaI	0.63	0.68	RbI	0.69	0.71
KF	0.95	0.94	CsF	0.99	0.96
KCl	0.83	0.83	CsCl	0.87	0.86
KBr	0.79	0.80	CsBr	0.83	0.83
KI	0.66	0.69	CsI	0.71	0.72

However, such a position occurs only for ideal crystal structures of the type of ZnS, NaCl, CsCl, etc., in which the coordination number (C.N.) is known precisely. When the coordination polyhedron is distorted, the distances from the centre to the various vertices in it differ appreciably, which raises the question of how the C.N. is to be used in calculating the bond ionicity. The difficulty in choosing the C.N. for calculating bond ionicities in crystals with irregular coordination polyhedra has been discussed in the literature.[108,157]

The escape from this position can be twofold: either the theoretical calculation of effective C.N. taking into account the non-equivalence of the bonds between the central atom and various ligands[158–163], or an empirical allowance for the real coordination of the atoms in the crystal. In the latter approach we[164] used the sublimation energy of the crystal (ΔH_S), since it is just this that distinguishes a molecular from a crystalline compound. Use of the sublimation energy permits going from the electronegativity of atoms for molecules to the electronegativities of atoms for crystals (X^*). To do this the well-known Pauling equation:

$$\Delta X_{AB} = 0.208\,[\Delta E(AB)]^{1/2}$$

is transformed into the form:

$$\Delta X^*_{AB} = 0.208\,[\Delta E(AB) + \Delta H_s]^{1/2} \quad . \qquad (22)$$

Combination of this equation with formula (5) gives the following expression:

$$\Delta\Delta X = \Delta X^*_{AB} - \Delta X_{AB} = 0.208\{[\Delta E(AB) + \Delta H_s]^{1/2} - [\Delta E(AB)^{1/2}]\} \quad , \qquad (23)$$

which allows the difference in the electronegativities of the atoms for the molecular and crystalline states to be calculated, and hence also the electronegativity of the atom for the crystalline state if the problem of which of the partners in the bond A–B is responsible for the change in electronegativity on going from the molecular to the crystalline state can be solved. Since the enthalpies of sublimation of the elements playing the part of anions are significantly less than those of metals, clearly the influence of the ΔH_S should appear mainly on the electronegativity of the cation. The results of such calculations of the electronegativities of the atoms in crystals have been given[164].

The electronegativities of the atoms in crystals can also be calculated from the electronic work function (Φ). Stevenson[165] suggested that the electronegativities of atoms of metals in the crystalline state could be calculated by the equation:

$$X^* = 0.355\Phi \quad . \qquad (24)$$

Later[166] the coefficient in Eqn.(24) was changed to 0.318 and the electronegativities of the atoms of almost all metals in the crystalline state were calculated. It was found that electronegativity$_{met}$ < electronegativity$_{mol}$, which is explained by the greater screening of the nuclear charge of atoms in the solid state compared with that of an atom in a molecule.

The closest approaches to thermodynamic values of the electronegativities of atoms in the crystalline state are obtained in calculations with the formula:

$$X^* = 0.4\Phi - 0.5 \quad . \qquad (25)$$

The values of the electronic work function for pure metals corrected from the enthalpies of formation of intermetallic compounds were used[167–172] for interpreting the structure and properties of metallic phases.

In using methods of calculating the electronegativities of atoms in crystals starting from geometric considerations, then in equations of type (7) instead of the usual covalent radius it is necessary to use the covalent radius of the same atom for the crystalline state and to allow also for the bond multiplicities in coordination crystals (cf. Batsanov[164]). The calculation of the electronegativities of atoms in crystals by a method similar to that of Sanderson but based on Fermi statistics has also been described; the results of these calculations agree well with the independent determinations of the electronegativities of corresponding atoms[173]. The optical determination of the electronegativities of atoms in crystals has been described[56,58,59].

Table 10 gives the system of electronegativities of atoms in crystals, averaged from the results of various methods.

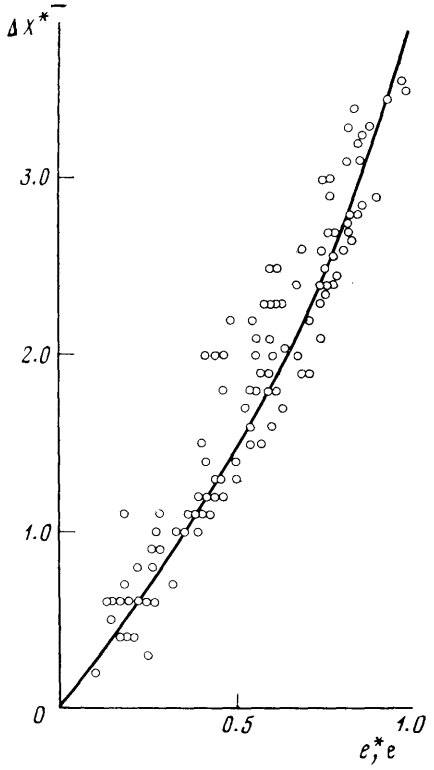


Figure 1. Variation of the effective charges of the atoms according to Szigeti with the differences of the electronegativities of atoms in crystals.

Table 10. System of electronegativities of atoms in crystals.

Period	1A	2A	3A	4A	5A	6A	7A	8A	1B	2B	3B	4B	5B	6B	7B
II	Li 0.6	Be 1.1									B 1.7	C 2.4	N 2.8	O 3.2	F 3.9
III	Na 0.5	Mg 0.9									Al 1.4	Si 1.6	P 2.0	S 2.4	Cl 3.2
IV	K 0.4_5	Ca 0.7	Sc 1.0	Ti 1.2	V (II) 1.2 (III) 1.5	Cr (II) 1.2 (III) 1.4 (IV) 1.6	Mn (II) 1.2 (III) 1.3 (IV) 1.5	Fe (II) 1.2 (III) 1.4	Co 1.2 1.4	Ni 1.2 1.4	Cu (I) 1.0 (II) 1.4	Zn 1.2	Ga 1.4	Ge 1.7	As 1.8	Se 2.3	Br 3.0
V	Rb 0.4	Sr 0.6_5	Y 0.9	Zr 1.1	Nb (III) 1.2 (V) 1.5	Mo (III) 1.2 (IV) 1.4	Tc (IV) 1.4	Ru (II) 1.3 (IV) 1.5	Rh 1.4 1.6	Pd 1.4 1.6	Ag 1.0	Cd 1.1	In 1.4	Sn (II) 1.4 (IV) 1.7	Sb (III) 1.5 (V) 2.0	Te 2.2	I 2.8
VI	Cs 0.3_5	Ba 0.6	La* 0.9	Hf 1.1	Ta (III) 1.1 (IV) 1.5	W (III) 1.2 (IV) 1.4	Re (IV) 1.5	Os (II) 1.3 (IV) 1.6	Ir 1.4 1.6	Pt 1.5 1.7	Au (I) 1.1 (III) 1.7	Hg 1.3	Tl (I) 1.1 (III) 1.5	Pb (II) 1.3 (IV) 1.8	Bi (III) 1.4 (V) 2.0	Po 2.0	At 2.4
VII	Fr 0.3	Ra 0.5_5	Ac 0.8												
	Actinides			Th (IV) 0.9	Pa (IV) 0.9 (V) 1.3	U (IV) 1.0 (V) 1.4 (VI) 1.7									

* $X_{Ln(II)} = 0.8$; $X_{Ln(IV)} = 1.0$.

On constructing graphs of the effective charges of atoms in crystalline compounds (Tables 5 and 6) against the difference in the electronegativities of the corresponding atoms (Fig.1), then the best curve obtained by the least squares method, can be used to find the function $i_{cr}(\Delta X)$, which allows the effective charges of atoms in crystals to be estimated. Table 11 gives the numerical values of the bond ionicities in the molecules, from formula (10), and in crystals as a function of ΔX.

The discrepancy between the experimental and calculated (Tables 10 and 11) effective charges of the atoms averages ±0.05 e or 10% of the absolute value of e^*. The exceptions are certain compounds of the B subgroups, for example, Cu, Ag, and Tl.

Table 11. Variation of the bond ionicity (%) with the difference in the electronegativities of the atoms.

ΔX	i_{mol}	i_{cr}	ΔX	i_{mol}	i_{cr}	ΔX	i_{mol}	i_{cr}	ΔX	i_{mol}	i_{cr}
0.1	1	4	1.0	20	36	2.0	51	64	3.0	80	85
0.2	2	8	1.2	26	42	2.2	58	69	3.2	84	88
0.4	5	16	1.4	32	48	2.4	64	73	3.4	88	91
0.6	9	23	1.6	38	54	2.6	70	77	3.6	91	94
0.8	14	29	1.8	44	59	2.8	75	81	3.8	93	97

The question of the reasons for this exception were recently considered by the example of compounds of the AB type[174]. The widely held opinion that the bonds for compounds of the B subgroup metals are more covalent than those for the compounds of the corresponding analogues in the A subgroups is based on the peculiarities of the geometric structure, the significantly different atomisation energies and melting points, the solubilities of the corresponding salts in water, and other physicochemical properties. In addition, the effective charges of the atoms determined by Eqn.(14) for Cu, Ag, Tl, and Pb halides are higher than for their analogues from the A subgroups. In the first stages of the development of the Szigeti method this circumstance even cast doubt on the legitimacy of the approach itself. However attention was subsequently paid to the following circumstance.

When valency is treated in the classical approach as the number of electrons provided by a given atom for the formation of chemical bonds, then can Cu be regarded as univalent in CuCl, and Pb as bivalent in $PbBr_2$? In fact, the energy of atomisation of univalent metals of the A subgroup K, Rb, and Cs are 21.3, 19.3, and 18.2 kcal $mole^{-1}$ respectively, whereas their analogues in the B subgroup Cu, Ag, and Au have energies of 80.7, 68.1, and 88.2 kcal $mole^{-1}$ respectively[175]. This difference is due to additional metal–metal bonds, which are formed by the atoms of elements of the copper subgroup in the solid state. According to Pauling[23], these elements in the pure metallic state have effective valencies (owing to the use of the *d*-electrons of the preceding layer), equal to $\nu^* = 5.6$. Coulson[141] in comparing the atoms Na and Cu, notes that the 3*d*-orbitals of neighbouring Cu atoms are overlapped much more strongly than the 2*p*-orbitals of the Na atoms. Therefore for copper it is impossible to think that bonds are formed exclusively with the aid of 4*s*-electrons. On taking into account the features of the zone structure of the copper and silver halides other investigators[83,176] took the effective valency of Cu and Ag to be 1.5. The valency (z) is in the denominator of Eqn.(14) and on dividing the experimentally determined effective charges in the copper and silver polyhalides by 1.5, this leads to an approach between the experimental and calculated values of the bond ionicities in these compounds. An X-ray spectroscopic investigation[177] confirmed the theoretical estimates.

The problem of the increased formal valency due to the participation of the lone electron pairs in the chemical bonds was investigated in the lead dihalides. As already mentioned, Axe and coworkers[124] were the first to suggest that the 6*s*-electrons of lead participate in the chemical bonds in compounds of the $PbHal_2$ type. Investigations of the electron structure of the lead dihalides[178–181] confirmed that the 6*s*-electrons of the Pb atom interact with the *p*-orbitals of the halogen atoms, and only on allowing for this interaction do the calculated bond polarities agree with those determined experimentally.

The above results of the theoretical and experimental investigations pose the important question of what is the real valency of the atoms in crystalline compounds and whether in the interpretation of physicochemical parameters we are restricted to only the formal valencies. A possible way of settling this question could be the comparison of the effective charges of atoms in crystals determined experimentally by the Szigeti method and estimated theoretically, for example, by the electronegativity method. A marked discrepancy between the results from these approaches will show the necessity of allowing for additional interactions of the atoms.

In the papers cited above[174] in addition to Cu, Ag, and Tl halides the chalcogenides of the metals of the zinc subgroup and the compounds of Ga and In with the group V elements are also considered. The mean effective valencies of the metals of subgroups IB–IIIB in compounds of AB type are 1.5, 2.4, and 3.1 respectively; that is, they increase with participation of the $(n-1)d$-electrons in comparison with the formal valency. The simple division of the effective charges of the atoms of the corresponding elements in crystalline compounds (listed in Table 5) by these quantities greatly improves the agreement between the experimental results and those calculated by the electronegativity method.

VI. THE PHILLIPS–VAN VECHTEN ZONE THEORY, BOND IONICITY AND THE STRUCTURE OF CRYSTALS

The Szigeti method gives good results in studying the nature of chemical bonds in dielectrics—ionic-covalent crystals. Essentially, it is based on the assumption of the total localisation of the valence electrons on the atom-partners of the chemical bond and does not take into account the possibility of the appearance of even a partly metallic character at the chemical bond of a crystalline compound.

The approach described in the present section, on the other hand, is based on the assumption that all the valence (outer) electrons of atoms in crystals are delocalised just as happens in metals and the laws of an electronic gas are applicable to them. In accordance with the Penn theory[182]:

$$n^2 = 1 + (h\nu_p/E_g)^2 , \qquad (26)$$

where E_g is the distance between the centres of the valence zone and the conductivity zone (Fig.2), and ν_p the plasma frequency of the vibrations of the valence electrons:

$$\nu_p = (4\pi e^2 N/mV)^{1/2} . \qquad (27)$$

Here N is the number of valence electrons, m their mass, and V the volume of the formula unit of the crystal.

Phillips[42,183–188] and van Vechten[186,187,189] developed, on the basis of these relations, the "dielectric theory of a chemical bond". On writing Eqn.(28) for such elements as diamond and silicon, then for them

$$\varepsilon = n^2 \quad \text{and} \quad E_g = E_{gc},$$

where the index "c" denotes a covalent crystal:

$$\varepsilon = 1 + (h\nu_p/E_{gc})^2 \ . \qquad (28)$$

On assuming that Eqn.(28) is valid for all crystals and that the value of E_g is made up of ionic (E_{gi}) and covalent (E_{gc}) terms, Phillips deduced the equation:

$$E_g^2 = E_{gc}^2 + E_{gi}^2 \ . \qquad (29)$$

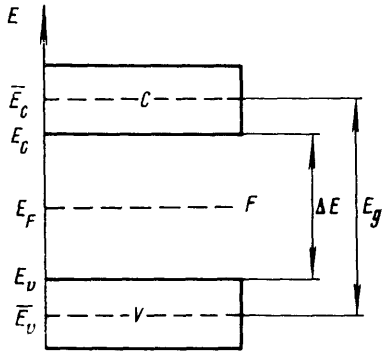


Figure 2. Schematic representation of the zone structure of crystals according to Phillips: V and C are the valence zone and conductivity zone, ΔE is the band gap, E_g the mean energy of transition of the valence electrons into the conductivity zone, and F the Fermi level.

It should be noted that before Phillips the papers of Suchet[190] and Batsanov[191] had already calculated the width of the zone gap of semiconductors from ionic and covalent components; however, Phillips approach is better based physically, which provided a possibility of obtaining fundamental results.

Since the use of Eqns.(26) and (28) led to values in good agreement with experiment, it became possible to determine E_{gi} on the basis of relation (29). Analysis of values of E_{gi} obtained empirically established that these characteristics can be presented as functions of the charges and radii of the atoms:

$$E_{gi}(\mathrm{AB}) = 1.5\left(\frac{z_A e^2}{r_A} - \frac{z_B e^2}{r_B}\right) e^{-k_s r} \ , \qquad (30)$$

where z_A and z_B are the valencies and r_A and r_B the radii of atoms A and B, $r = \frac{1}{2}(r_A + r_B)$, and k_s is the Thomas–Fermi screening factor. The last term ($e^{-k_s r}$) signifies that the valence electrons in a semiconducting crystal are considered to be free (as in metals) and therefore Thomas–Fermi statistics are completely applicable to them.

Expression (30) provided Phillips[188] with a basis for calculating the electronegativities of atoms by the formula:

$$X = 4.0\,(z/r)\,e^{-k_s r} + 0.5 \ , \qquad (31)$$

in which the coefficients 4.0 and 0.5 were chosen so that the Pauling scale was satisfied for the elements C and N. The results of the calculations by formula (31) have been published[47,192,193].

According to Phillips, the bond ionicity in a crystal is determined on the basis of Eqn.(29) by the formula:

$$f_i = E_{gi}^2/E_g^2 \ . \qquad (32)$$

Results of calculations by this formula are given in Tables 12 and 13.

Table 12. Bond ionicity (%) in crystals of type AB (according to Phillips).

A (I)	B (I)			
	F	Cl	Br	I
Li	91	90	90	89
Na	95	94	93	93
K	95	95	95	95
Rb	96	96	96	95
Cs	—	96	96	96
Cu	—	88	88	86
Ag	—	96	93	90
Tl	94	94	94	93
A (II)	**B (II)**			
	O	S	Se	Te
Be	62	61	61	59
Mg	84	79	79	59
Ca	92	91	90	90
Sr	93	92	92	91
Ba	93	93	94	94
Zn	65	62	62	60
Cd	78	68	68	67
Hg	—	70	5	5
Ge [197]	—	—	68	52
Sn [198]	84	76	72	64
Pb [198]	86	79	76	65
Mn	89	78	68 *	55 *
A (III)	**B (III)**			
	N	P	As	Sb
B	26	6	3	
Al	44	39	43	43
Ga	45	33	31	26
In	50	42	36	33

Kolmykov[194] carried out an interesting transformation of the Phillips equations. On taking the unity over to the left-hand side of each equation (26) and (28), and then dividing one equation by the other, we obtain:

$$\frac{n^2 - 1}{\varepsilon - 1} = \frac{E_{gc}^2}{E_g^2} = f_c \ , \qquad (33)$$

where

$$f_c = 1 - f_i.$$

Hence

$$f_i = \frac{\varepsilon - n^2}{\varepsilon - 1} \ . \qquad (34)$$

Calculation by Eqn.(34) is the simplest method of calculating the bond ionicity according to Phillips.

In the initial Phillips–van Vechten theory the value of f_i was calculated for crystals of the ZnS and NaCl structure types consisting of sp-elements. Subsequently, the theory was extended to crystals of other structure types and to d-elements. A significant contribution to the dielectric theory was made by Levin[195,196] who in calculating the number of valence ("plasma") electrons for the B subgroup elements took into account all $(n-1)d$-electrons, and not only the ns- and np-electrons. This interpretation is similar to that used in calculating the effective charges of the atoms

of the *d*-elements according to Szigeti. Levin demonstrated very convincingly the correctness of this approach for the example of Cu_2O, where in allowing for only the 4*s*-electron of copper $f_i \cong 0$ is obtained and only when all the 3*d*-electrons are included in the number of plasma electrons was $f_i = 0.56$ e obtained.

Tables 12 and 13 give the Phillips bond ionicities obtained by Levin and also those we have calculated by Eqn.(34) (the latter values are marked by an asterisk).

Table 13. Bond ionicity (%) in crystals of type A_nB_m (according to Phillips).

AB_2	f_i	AB_3	f_i	A_2B_3	f_i
MgF_2	91	SiO_2	57	Al_2O_3	80
CaF_2	97	Ge^4O_2	51	Cr_2O_3	78
SrF_2	97	Ge^6O_2	73	Fe_2O_3	68
BaF_2	97	SnO_2	75*	As_2S_3	29*
ZnF_2	89	SnS_2	49*	As_2Se_3	28*
CdF_2	93	$SnSe_2$	44*		
$CdCl_2$	66*	TiO_2	94*		
$CdBr_2$	68*	TiS_2	84*		
CdI_2	68*	$TiSe_2$	69*		
PbF_2	94	ZrS_2	75*		
PbI_2	80	HfS_2	76*		
		$HfSe_2$	81*		

Comparison of the results in Tables 12 and 13 and Tables 5 and 6 shows that the bond ionicities determined by the Szigeti and the Phillips methods are not the same. The physical reason for the differences was discussed above and we will now consider the interconnection between i (Pauling–Szigeti method) and f_i (Phillips method).

Lawaetz[176] found that

$$e^*/z \sim E_{gi}/h\nu_p.$$

Hence by using Eqn.(26) Uemil[192] obtained the expression:

$$(e^*/z)^2 \sim f_i/(n^2-1) \quad . \tag{35}$$

The physical significance of this relation is completely understandable, since the charges according to Szigeti are identical to the Pauling bond ionicity and the latter, according to Eqn.(11), is determined by the energies, whereas the charges according to Phillips depend on the square of the energy—cf. also the exponent of the powers of $(\varepsilon - n^2)$ in Eqns.(14) and (34).

The Phillips–van Vechten theory was modified in several subsequent studies. Thus Unger and Neumann[200] found that

$$f_i = \frac{1}{2}\left(1 - \cos\pi\frac{E_{as}}{E_{vb}}\right) \tag{36}$$

where E_{as} is the antisymmetric energy gap [within the valence band (Ed. of Translation)] and E_{vb} the total valence band width of the crystal. Later the same formula was used by Hübner[201,202] for calculating the bond ionicities in a series of transition metal oxides and halides.

Hübner also considered the application of the Phillips–van Vechten method to amorphous materials. Since according to Phillips

$$E_{gi} \backsimeq r^{-1}, \quad E_{gc} \backsimeq r^{-2.5} \tag{37}$$

it is easy to see that

$$\begin{aligned} E_{gc}^2(\text{am}) &= E_{gc}^2(\text{cr})\,(\rho_{\text{am}}/\rho_{\text{cr}})^{5/3}, \\ E_{gi}^2(\text{am}) &= E_{gi}^2(\text{cr})\,(\rho_{\text{am}}/\rho_{\text{cr}})^{2/3}, \\ \nu_p^2(\text{am}) &= \nu_p^2(\text{cr})\,(\rho_{\text{am}}/\rho_{\text{cr}}) \end{aligned} \tag{38}$$

where ρ_{am} and ρ_{cr} are the densities of the amorphous and crystalline phases. The dielectric constants of amorphous substances calculated by these formulae agree satisfactorily with experiment.

Hübner[203] investigated in special detail the bond ionicity in various forms of SiO_2 crystals. He found that the refractive index of silicon dioxide obeys the equation:

$$n = 1.04 + 0.19\,\rho,$$

where ρ is the density of various modifications of SiO_2. On taking into account that $\nu\rho \cong \rho$, we obtain:

$$n = [1 + (n_\alpha^2 - 1)\,\rho/\rho_\alpha]^{1/2} \tag{39}$$

where the subscript α denotes α-quartz. Later, Hübner obtained the formula:

$$n^2 = 1 + 1.26r^2(1 - f_i) \tag{40}$$

where r is the minimal Si–O distance in the corresponding structure. Hence the following values are obtained for f_i: α-quartz 0.57; β-quartz 0.60; α-tridymite 0.59; α-cristobalite 0.58; β-cristobalite 0.61; coesite 0.53; keatite 0.59; glass 0.65.

A new variant of the Phillips formula was proposed[204]:

$$f_i = V_a^2/(V_s^2 + V_a^2), \tag{41}$$

where V_a and V_s are antisymmetric and symmetric form-factors of the potential of the crystal which are determined from the value of E_g. Comparison of the results obtained by Eqn.(41) with Phillips' results shows their agreement.

In conclusion, we note that the Phillips–van Vechten theory went firmly into the arsenal of the methods of solid-state quantum chemistry and physics, and it is now difficult to list all the studies where the dielectric theory of the chemical bond is used or developed. The present review surveys only the main works on this method of studying the chemical bond in crystals. Additional information can be obtained elsewhere[192,196,205–207].

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Having considered the history and contemporary state of the use of dielectric methods in studying the nature of the chemical bond in chemical substances in any state of aggregation, it is easy to be persuaded that the information obtained with this method is in complete agreement with structural theory and with the results of independent methods of investigating bond polarities. The relative simplicity and rapidity of the measurements, together with their universality and low requirements for the quality of the test specimens makes this method extremely attractive for chemists.

For the future, the most interesting problem is the study of changes in the nature of the chemical bond at high pressures (up to the transformation of a dielectric into the metallic state).

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