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The Problem of Monatomic Multicharged Ions and the Nature of the Chemical Bond in Inorganic Crystals

A.A.Levin, Ya.K.Syrkin, and M.E.Dyatkina

The review deals with the problem of the chemical bond in inorganic solids on the basis of the analysis of the experimental data. It is shown that thermochemical and crystal-chemical arguments can hardly be regarded as proof of the ionic theory, while data derived by modern methods for the direct estimate of effective charges show quite definitely that the bonds are covalent even in structures such as alkaline earth metal oxides and chalcogenides. The bibliography comprises 116 references.

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I. INTRODUCTION

The aim of the present review is to examine the present state of the problem of the nature of the chemical bond in inorganic crystals. Although the concept of the partial covalence of such crystals has now become fairly widespread[1-3], the tendency to regard this "covalent component" as a relatively small correction to the ionic state predominates. One of the reasons for this situation is the traditional belief that the classical ionic theory and its concepts of multicharged ions are consistent with the majority of thermochemical and crystal-chemical data, which are thus regarded as "proof" of the validity of this theory. More detailed analysis shows, however, that in all cases, except alkali metal halides, thermochemical and crystal-chemical arguments are not convincing and in fact it is not experimental data that are consistent with the ionic theory but certain theoretical postulates in the thermochemistry of crystal lattices and in crystal chemistry—branches of science which have developed for half a century under the dominant influence of the ionic concept. Therefore such agreement is not surprising, but, rather than being the foundation of the ionic model, it is its consequence. The relevant questions have been examined in sections II and III of the present review.

On the other hand a fairly large amount of direct experimental data on charge distribution in inorganic solids has now accumulated. These experimental results show that the only inorganic crystalline materials close to a purely ionic state are probably alkali metal halides, for which the ionic theory holds almost completely. In crystals of compounds of "polyvalent" elements the effective charges do not increase but are actually more likely to decrease with increase in formal valence. Thus the effective ionic charges in alkaline earth metal oxides and chalcogenides ($A^{II}B^{VI}$) do not exceed unity in all probability† and in compounds of the type $A^{III}B^{V}$ they are approximately 0.5. In

† However, many workers continue to regard these crystals as purely ionic[4].

compounds more complex than the binary compounds with the composition AB the situation is somewhat more complicated but even in crystals of this kind the effective ionic charges are low‡. Experiments show that the anionic charges never exceed about 1 e, while cationic charges may be somewhat greater. Experimental data on the effective charges are considered in section IV.

The review concludes with section V, where the question of the possible physical cause limiting the effective charge of the atom in a molecule or crystal is discussed. The concluding paragraph deals with the problem of the quantum-mechanical description of the partially covalent state in solids. A fairly typical example, showing how an appreciable departure from a purely ionic structure can lead to a considerable change in the physical properties of the solid, is also quoted there.

II. THERMOCHEMICAL DATA AND THE PROBLEM OF MULTICHARGED IONS

The fundamental thermochemical concept in ionic theory is the so called "lattice energy" (Table 1), i.e. the energy which would be evolved in a hypothetical process involving the mutual approach of ions (including multicharged ions) from infinity to real atomic distances in the crystal. Two properties are then used as the main evidence in favour of the ionic model (Table 1): (1) the similarity of the "theoretical" and "experimental" lattice energies; (2) the sharp increase in lattice energy on going from compounds of "univalent" elements to compounds of "polyvalent" elements, in full agreement with the quadratic relation between the energy of electrostatic attraction and the charge.

Table 1. Theoretical (U_T) and experimental (U_E) lattice energies in crystals*

Crystal	U_T, kcal mole^{-1}	U_E, kcal mole^{-1}	Q, kcal mole^{-1}	E_{atom}, kcal mole^{-1}
NaF	217 [5]	217 [7]	136	180
KF	193 [5]	193 [7]	134	174
RbF	184 [5]	185 [7]	131	170
CsF	176 [5]	173 [7]	127	164
NaCl	185 [5]	185 [7]	98	152
KCl	168 [5]	169 [7]	104	154
RbCl	161 [5]	162 [7]	103	152
MgO	942 [6]	942 [6]	144	239
CaO	865 [6]	853 [6]	152	257
SrO			141	239
BaO	756 [6]	766 [6]	133	235
MgS	807 [6]		83	178
CaS	740 [6]		115	220
SrS	696 [6]		108	200

* The heats of formation (Q) of the compounds and the heats of sublimation of the metals taken from Ref. 8 and the dissociation energies of diatomic molecules taken from the summarising table in Ref. 16 were used to calculate the atomisation energy E_{atom}. Here and henceforth literature references are quoted immediately after the numerical data.

‡ It is superfluous to emphasise that the concept of the essentially covalent structure of inorganic crystals in no way contradicts the generally known experimental facts, for example, Faraday's laws of electrolysis. Furthermore, in solutions we are dealing not with atomic but with solvated ions.

However, simple analysis shows that for compounds of "polyvalent" elements both these properties do not reflect any experimental relations but are a consequence of the definition of the concept of the "theoretical" lattice energy, which is calculated precisely on the basis of the postulate of the ionic nature of the bond.

1. Theoretical Lattice Energy

The theoretical lattice energy U_T is by definition a purely computational quantity which can be formally calculated for any system of real or fictitious charges. Nevertheless the use of this concept in the theory of crystal lattices already involves certain difficulties.

Even within the framework of the postulated ionic model U_T cannot be calculated unambiguously, since in the expression for the theoretical lattice energy§

$$U_T = \frac{MZ^2}{R} - U_{rep.}, \qquad (1)$$

the electrostatic bond mechanism defines only the first term $U_{electr} = MZ^2/R$. The exact form of the second term U_{rep} is unknown (it is specified by the expression for the potential V_{rep}, which takes into account the repulsion between ions at distances smaller than the equilibrium value). Usually any one of the model functions of the following types is employed for the "repulsion" potential:

$$\begin{aligned} &\text{(a) } V_{rep.} = br^{-n} && \text{Born and Lande [9]},\\ &\text{(b) } V_{rep.} = be^{-ar} && \text{Born and Mayer [10]},\\ &\text{(c) } V_{rep.} = \varepsilon + be^{-ar} + cr^{-6} + dr^{-8} && \text{Ladd and Lee [11]}, \end{aligned} \qquad (2)$$

but none of these has a rigorous theoretical foundation and therefore none has any advantages over the others¶. However, the use of different functions (and different parameters a, b, and c, ...) leads to appreciable discrepancies in the corresponding values of U_T (Table 2). This discrepancy amounts to only 1–2 kcal mole^{-1} for alkali metal halides, but increases by a factor of several tens for other compounds.

Table 2. Theoretical lattice energy U_T of crystals according to different calculations

Crystal	Na_2O	K_2O	Rb_2O	MgO	CaO	BaO	ZnO	GeO_2	SnO_2	TiO_2
U_T, kcal mole^{-1}	651 [5]	580 [5]	552 [5]	942 [6]	865 [6]	756 [6]	990 [15]	2534 [18]	2301 [18]	2429 [18]
	600 [17]	529 [17]	508 [19]	907 *	816 *	726 *	917 [19]	3210 [19]	2845 [19]	2958 [19]

* From Ref. 32, Vol. I; according to Baughan's data [14].

§ Here Z is the formal ionic charge, R the anion–cation interatomic distance, and M the Madelung constant, which is 1.64 for a ZnS type lattice and 1.75 for an NaCl type lattice. Eqn. (1) is written in terms of atomic units.

¶ Sometimes it is suggested that Eqn. (b) follows from quantum mechanics and therefore is more justified, than, for example, Eqn. (a). In fact Eqn. (b) is a simplified version of the formula obtained by Unsöld [12] and Brück [13] for the repulsion potential between a positive point charge and a hydrogen-like atom and cannot be applied to real crystals.

The attempts to calculate U_T for the ionic model by the more correct quantum-mechanical procedure also proved to be comparatively successful only for alkali metal halides [20-23]. The results of the calculation [24] for MgO by the same method [20-23] using Watson's functions [25] for O^{2-} ions agree with elementary electrostatic calculations (Tables 1 and 2) only to a first approximation: $U_T^{(1)} = 923$ kcal mole^{-1} and the equilibrium lattice constant $a^{(1)} = 4.23$ Å. In calculations based on a second approximation it was found unexpectedly that the mutual repulsion of ions, which had always been neglected, exceeds in fact by a factor of 2-3 (!) the Born repulsion between anions and cations, so that the more accurate calculation leads to much poorer results: $U_T^{(2)} = 747$ kcal mole^{-1} and the lattice constant $a^{(2)} = 5.5$ Å (against the experimental value $a = 4.21$ Å)†.

2. Experimental Lattice Energy

In the discussion of experimental lattice energies, U_E it is necessary to consider two cases which differ sharply in their physical significance. For compounds of "univalent" elements, U_E is determined with the aid of the Born-Haber cycle from the equation

$$U_э = Q + S + \tfrac{1}{2}D + I_1 - F_1 \qquad (3)$$

where Q is the heat of formation of the compound AB, S the heat of sublimation of the metal A, D the heat of dissociation of the molecule B_2, I_1 the first ionisation potential of the metal A atom, and F_1 the affinity of the non-metal B atom for one electron. For compounds $A^{I}B^{VII}$, all the quantities on the right-hand side of Eqn. (3) are susceptible to direct experimental determination regardless of any hypotheses concerning the nature of the bond between the atoms in the crystal. Thus the heats Q, S, and D and I_1 are obtained by direct thermochemical and spectroscopic measurements [26,27], and the affinity for one electron F_1 can be determined, for example, from data on light-induced ejection of an electron [28]. Therefore in the case of alkali metal halides U_E is a purely experimental quantity and the agreement between U_T and U_E indeed means that the corresponding crystals can be regarded as constructed from the ions Li^+, Na^+, ..., F^-, Cl^-, ...

The situation is quite different for compounds of "polyvalent" elements for example the oxides and chalcogenides of alkaline earth metals or transition metals: Mg, Ca, Ti, V, etc. In this case the "experimental" lattice energy is defined thus:

$$U_E = Q + S + \tfrac{1}{2}D + I_1 + I_2 - F_1 - F_2 \ . \qquad (4)$$

At first sight this expression is constructed in the same way as that for univalent elements. However, in fact there is a profound difference between Eqns. (3) and (4).

† It is remarkable that when account was taken of the repulsion between anions in the calculation of Peterson et al. [23] for sodium chloride, poor agreement between the values of U_T and U_E was again obtained. Thus the calculation to first-order approximation gave $U_T^{(1)}$ (NaCl) = 183 kcal mole^{-1} and $A^{(1)} = 5.4$ Å, while the calculation to second-order approximation (taking into account the repulsion between Cl^- ions) gave $U_T^{(2)}$ (NaCl) = 155 kcal mole^{-1} and $a^{(2)} = 6.77$ Å.

The quantity U_E calculated from Eqn. (4) cannot be regarded as the result of an experimental (if only in principle) Born-Haber cycle, i.e. as a physical quantity susceptible to experimental measurements, since Eqn. (4) includes together with experimentally measured quantities Q, S, D, I_1, I_2, and F_1 also a quantity of a significantly different type. This quantity is the affinity of the atom for a second electron (F_2), which cannot be found by any independent method.

3. Affinity of the Atom for Several Electrons

The reason why F_2 cannot be determined is due to the fact that the affinity for a second electron would have to be understood as the energy of the process

$$B^- + e^- \rightarrow B^{2-} + F_2 \qquad (5)$$

which in reality never takes place‡. The experimental data show that for free atoms such a process cannot in fact occur since the binding energy of even one "superfluous" electron in the singly charged ions O^-, S^-, etc. is low (see section V, 1). On the other hand, there are no direct experimental data which would indicate the existence of monatomic multicharged negative ions in molecules or crystals (see section IV) and theoretical considerations also cast doubt on their existence (see section V).

It is noteworthy that although the concept of affinity for several electrons is usually associated with the thermochemistry of crystal lattices, real thermochemical data by themselves, without the previously adopted ionic concept, do not require the introduction of such a concept at all. The heats of formation and atomisation energies of alkali metal halides and alkaline earth metal oxides and chalcogenides are compared in Table 1. It is evident from this table that the heats of formation of the chalcogenides are close to the heats of formation of the halides and are in no way comparable to the enormous "lattice energies" for doubly charged ions§. Thus the only reason for the introduction of the concept of affinity for several electrons was the attempt to compensate the excessively large attraction energy of multicharged ions in the ionic model, i.e. essentially to adjust the experimental heats of formation to the postulates of the ionic theory (very large negative values must be attributed to the affinity for several electrons [32]).

4. The Reason for the Agreement Between the "Experimental" and "Theoretical" Lattice Energies

The vicious circle indicated above makes it impossible to find U_{exp} by an experimental procedure even within the framework of the ionic model. In order to escape from this vicious circle, it is usually postulated in the ionic

‡ From the standpoint of quantum mechanics, extremely unstable doubly charged ions with a lifetime of the order of 10^{-10} s are possible [29]. According to some data, such ions (with a lifetime of about 10^{-4} s) were recently observed mass-spectrometrically [30], although in another paper [31] doubt was cast on these results. At any rate the presence of such unstable species in no way supports the ionic theory, particularly since doubly charged ions F^{2-}, Cl^{2-}, and Br^{2-} with the same lifetime were observed together with O^{2-} in this investigation [30].

§ The difference between the atomisation energies is of course greater. However, it too is insignificant compared with the difference between the lattice energies.

theory that crystals have a purely ionic structure, and that in Eqn. (4) for any one compound adopted as a standard it is possible to substitute U_T for U_E. Then the corresponding "affinity for two electrons":

$$F_1^0 + F_2^0 = Q^0 + S^0 + \frac{1}{2}D + I_1^0 + I_2^0 - U_T^0 \qquad (6)$$

is adopted as the "experimental" value and is substituted in Born's cycle [formula (4)] for all other compounds. However, it is readily seen that U_E is then given by the equation

$$U_E = U_T^0 + (Q - Q^0) + (S - S^0) + (I_1 + I_2 - I_1^0 - I_2^0) = \qquad (7)$$
$$= U_T + (U_T^0 - U_T) + (Q - Q^0) + (S - S^0) + (I_1 + I_2 - I_1^0 - I_2^0) = U_T + \Delta U ,$$

where the sum of the quantities in brackets (ΔU) is small compared with the first term U_T¶. Thus Eqn. (7) shows that the so called "experimental" lattice energy U_E represents essentially the same "theoretical" energy U_T after it has been only slightly modified by experimental data. Therefore neither the order of magnitude of U_E nor the agreement between U_T and U_E reflect any experimental facts and of course cannot be regarded as proof of the ionic structure of the corresponding crystals.

Although Eqn. (7) makes it possible to explain in broad outline both the order of magnitude of U_E and the approximate agreement between U_E and U_T, it is frequently asserted that the "thermochemical" affinities for several electrons obtained for different lattices are so close that it is bound to imply the reality of multicharged ions. Therefore we shall consider the question of this agreement in detail (for oxygen as an example). In the first place, as shown by Eqn. (6), the quantity $F_1 + F_2$ is not purely experimental but depends on the value of U_T. Therefore, even for the same compound, $F_1 + F_2$ may assume different values depending on which formula is selected for the calculation of U_T. For example, the values of $F_1 + F_2$ for CaO calculated using the theoretical lattice energy[6] U_T(CaO) = 865 kcal mole^{-1} [6] (the Ladd–Lee formula) and the value[14] U_T(CaO) = 816 kcal mole^{-1} (the Born–Meyer formula) are respectively about −190 and about −140 kcal mole^{-1}, i.e. differ by 50 kcal mole^{-1}. A similar discrepancy is found when the same formula is used for different compounds, even when these are of the same structural type. Thus when the Born–Lande formula is applied to CaO, we have U_T = 852 kcal mole^{-1} [15,32] and then $F_1 + F_2$ = −177 kcal mole^{-1}, while for VO we have U_T = 996 kcal mole^{-1} [15,32] and $F_1 + F_2$ = (−220)–(−240) kcal mole^{-1} (the heat of formation of VO has evidently not been established exactly[33]). Consequently the "thermochemical" affinity of oxygen for two electrons can vary within extremely wide limits, from 140–150 kcal mole^{-1} [17,32] to 220–240 kcal mole^{-1} and therefore one can speak of the constancy of this affinity to within 10–15 kcal mole^{-1} only in a very restricted sense for a series of chemically and crystal-chemically similar compounds and under the condition that the same formula is used to calculate U_T.

However, in this case the constancy of the right-hand side of Eqn. (6) is not surprising. It is accounted for simply by the fact that in a series of such compounds the potentials I_1 and I_2 vary in parallel with $1/R_{cation} \propto 1/R \propto U_T$, whereas the heats Q vary within comparatively narrow limits (see, for example, Table 1).

¶ $Q - Q^0$ and $S - S^0$ are usually small (for alkaline earth metal oxides each of these does not exceed about 10 kcal mole^{-1}) and the quantities $U_T^0 - U_T$ and $I_1 + I - I_1^0 - I_2^0$ usually have different signs and cancel out.

5. "Thermochemical" and "Spectroscopic" Affinities for Several Electrons

The agreement between the "thermochemical" affinity for two electrons and the corresponding "spectroscopic" value is sometimes quoted as yet another argument in favour of the ionic theory. The "spectroscopic" value of F_2 is understood as the quantity found by the extrapolation of the spectroscopic values of the ionisation potentials and affinities for one electron and hence independent of lattice energy. However, such arguments, based on the "agreement" between $(F_2)_{thermochem}$ and $(F_2)_{spectr}$ can also be scarcely regarded as convincing. Indeed the "spectroscopic" value of F_2 as well as the "thermochemical" value are not constant but depend on the method of extrapolation. Thus extrapolation for the isoelectronic series from F^- to S^{6+} yields $F_1 + F_2$ = −155 kcal mole^{-1} for the oxygen atom[34]; Glockler's formula[35] $J = \alpha z^2 + \beta z + \gamma$ yields $F_2 \simeq$ −191 kcal mole^{-1},[36] while according to the data of Crossley and Coulson[37], the "spectroscopic" affinity of oxygen for two electrons is estimated as −118.6 kcal mole^{-1}. Since F_1 ranges from 23.5 to 46 kcal mole^{-1} according to different estimates (see Ref. 32, Vol. II), it follows that $(F_2)_{spectr}$ varies in the range 140–200 kcal mole^{-1} and the agreement of this value with $(F_2)_{thermochem}$, which varies in the range 140–220 (240) kcal mole^{-1} can be treated only as agreement with respect to the order of magnitude.

Finally, one must bear in mind that ionisation potentials and affinities for one electron correspond to bound states of the electron in the atom which are physically completely different from the free state corresponding to the hypothetical multicharged ion. From this standpoint, the extrapolation procedure itself for the determination of $(F_2)_{spectr}$ appears altogether fairly doubtful. On the other hand, if one assumes, in accordance with the ionic theory, that the structure of the energy levels of the atom in a compound changes radically, the multicharged ion passing into a bound state, then the use of the energy levels of the free atom in the extrapolation does not appear very logical.

Table 3. Comparison of the theoretical and experimental lattice energies for various crystals

Crystal	U_T, kcal mole^{-1}	U_E, kcal mole^{-1}	Q, kcal mole^{-1}	E_{atom}, kcal mole^{-1}	Crystal	U_T, kcal mole^{-1}	U_E, kcal mole^{-1}	Q, kcal mole^{-1}	E_{atom}, kcal mole^{-1}
ZnO	917	981	83	173	Cu_2O	656	794	40	262
ZnS	794	878	48	133	Cu_2S	555	706	19	235
ZnSe	753	864	34	114	Ag_2O	619	730	7	205
CdO	854	921	61	137	Ag_2S	528	663	8	199
CdS	746	827	34	105	Ag_2Se	518	658	3	189
HgO	828	944	22	96	Tl_2O	552	646	42	187
HgS	726	869	13–14	82	Tl_2S	491	557	21	160
HgSe	692	860	5	85	Tl_2Se	470	554	18	153
SnO	815	883	68	138	SiO_2	3280	3137	205	429
SnS	742	765	19	144	GeO_2	3210	3066	128	321
PbO	777	852	52	158	SnO_2	2301 [18]	2924 [18]	139	329
PbS	686	754	22	122	TiO_2	2429 [18]	2900 [18]	218	448
PbSe	655	750	18	115	MnO_2	3100 [40]	3670 [40]	124	311

* All the values of U_T and U_E, with the exception of those given individual references, were taken from Yatsimirskii[19]. The heats of formation Q of the compounds and the heats of sublimation of the metals were taken from Ref. 8; the heats of formation of silicon, germanium, and tin compounds were taken from Benson[39].

6. Thermochemical Arguments Against the Ionic Theory

As shown in subsections 3 and 5 in section II (mainly for alkaline earth metal oxides), thermochemical data can never be treated as proof of the ionic theory. For other compounds, the discrepancies between the thermochemical data and the predictions of the ionic model become so large† that they in fact turn into direct arguments against this model.

The theoretical and experimental lattice energies of a number of substances are compared in Table 3. The discrepancy between U_T and U_E reaches in this case an amount equal to the heat of formation of the compounds (or the affinity of the anions for two electrons, if this is preferable) and sometimes actually exceeds it. Evidently, in such a case one is dealing with a sharp discrepancy between experiment and the ionic model.

III. IONIC RADII AND CRYSTAL CHEMISTRY

Classical crystal chemistry with its central concept of ionic radius has always been regarded as closely related to the ionic model; therefore crystal-chemical arguments are usually advanced in favour of this model (see Ref. 41 for example). Three such arguments are most often discussed.

1. The possibility of employing ionic radii, including the radii of multicharged ions, to represent interatomic distances. [If the ions Mg^{2+} and O^{2-} do not exist, then why is $R(Mg^{2+}) + R(O^{2-}) = R(MgO)$?].

2. The relative dimensions of anions, cations, and neutral atoms. [The ionic radius of Mg^{2+} in the MgO structure is $R(Mg^{2+}) = 0.65$ Å and the atomic radius is $R(Mg) = 1.5$ Å; does this not demonstrate that all the valence electrons have been removed from the magnesium ion ?].

3. The possibility of explaining the crystal structure on the basis of the Magnus–Goldschmidt "stability limits" [radius ratio rules (Ed. of Translation)]. (Geometry shows that precisely six spheres with a radius of 1.40 Å can be accomodated around a sphere with a radius of 0.65 Å. Does this not confirm that magnesium and oxygen ions in the MgO crystal are spheres with precisely this radius ?).

We shall discuss these arguments in succession.

1. Anion–Cation Distances

The generally adopted ("classical") systems of ionic radii[42-50] are well known and agree with one another to within several hundredths of an ångstrom. One of these (Pauling's system) is quoted in the first column of Table 4. In any of these systems the sum of the radii $R(A^{n+}) + R(B^{n-})$ is equal to the interatomic distance and in this sense they all indeed "explain" the experimental data. The problem is, however, how unambiguously ionic radii may be obtained from experimental interatomic distances. We are restricting for the time being the discussion to anion–cation distances; it is easy to show that none of the "classical" scales does in fact follow from experimental data, since comparison of such interatomic distances can in general yield no information about the actual dimensions of the ions. The only experimental relation which follows from a comparison of interatomic distances is the approximate constancy of differences of the following type (Å):

$$\begin{aligned} &R\,(CaO) - R\,(MgO) = 0.30,\\ &R\,(CaS) - R\,(MgS) = 0.24,\\ &R\,(CaSe) - R\,(MgSe) = 0.23,\\ &\ldots\ldots\ldots\ldots \end{aligned} \tag{8}$$

or analogous differences for the same metal atoms (Å):

$$\begin{aligned} &R\,(MgS) - R\,(MgO) = 0.50,\\ &R\,(CaS) - R\,(CaO) = 0.44,\\ &R\,(SrS) - R(SrO) = 0.37,\\ &\ldots\ldots\ldots\ldots \end{aligned} \tag{9}$$

Table 4. Various systems of ionic radii (Å)

Pauling's ionic radii (Refs.47-49)		Slater's ionic radii (Refs.51 and 52)		Ionic radii from (Ref.53)		Ionic radii found by Pauling's rule [see (III),5)]	
Li^+	0.60	Li	1.45				
Na^+	0.95	Na	1.80				
K^+	1.33	K	2.20				
Rb^+	1.48	Rb	2.35				
Cs^+	1.69	Cs	2.60				
Be^{2+}	0.31	Be	1.05				
Mg^{2+}	0.65	Mg	1.50	Mg^+	1.35	Mg^+	1.25
Ca^{2+}	0.99	Ca	1.80	Ca^+	1.65	Ca^+	1.55
Sr^{2+}	1.13	Sr	2.00	Sr^+	1.82	Sr^+	1.62
Ba^{2+}	1.35	Ba	2.15	Ba^+	2.01	Ba^+	1.81
F^-	1.36	F	0.50				
Cl^-	1.81	Cl	1.00				
Br^-	1.95	Br	1.15				
I^-	2.16	I	1.40				
O^{2-}	1.40	O	0.60	O^-	0.75	O^-	0.88
S^{2-}	1.84	S	1.00	S^-	1.25	S^-	1.20
Se^{2-}	1.98	Se	1.15	Se^-	1.38	Se^-	1.35
Te^{2-}	2.21	Te	1.40	Te^-	1.40	Te^-	1.55

Eqns. (8) and (9) can perhaps be naturally interpreted as an indication of the approximate constancy of the "dimensions" of atoms—at least in a series of compounds similar in the chemical and crystal-chemical sense. However, even such an interpretation yields only the differences between the corresponding radii (Å):

$$\begin{aligned} &R\,(Ca) - R\,(Mg) = 0.23 - 0.30,\\ &\ldots\ldots\ldots\\ &R\,(S) - R\,(O) = 0.37 - 0.50\\ &\ldots\ldots \end{aligned} \tag{10}$$

and not the true "dimensions" of atoms or ions‡. The position does not change when instead of similar compounds one considers compounds belonging to different types (both in the chemical and crystal-chemical sense). As in the previous case, it is readily seen, that a comparison, for example, of the equations (Å)

$$\begin{aligned} &R\,(Mg) + R\,(O) = 2.10 && (\text{in MgO}),\\ &R\,(Na) + R\,(O) = 2.41 && (\text{in } Na_2O),\\ &R\,(Mg) + R\,(F) = 1.98\text{–}2.05 && (\text{in } MgF_2),\\ &R\,(Na) + R\,(F) = 2.31 && (\text{in NaF}) \end{aligned} \tag{11}$$

† Provided, of course, that one considers real values and is not satisfied with agreement between the fictitious quantities U_T and U_E to within 15 or 20%! A typical example of such an error is the calculation of the bonding energies of the Mn^{2+} and O^{2-} ions in the MnO crystal[38]. The Heitler–London method yields in this case U_T = 796 kcal mole^{-1}, which is regarded as satisfactory because of the good agreement with U_E = 923 kcal mole^{-1}. In fact the actual accuracy of the calculation is much lower, since the "theoretical" and "experimental" heats of formation differ by a factor of two.

‡ Eqns. (10) show, incidentally, that the very concept of ionic radius is at best valid only to within 0.1 Å. Therefore there is hardly much point in specifying any system of ionic radii with undue precision.

yields nothing except the differences between the ionic radii (Å):

$$\begin{aligned} R(\mathrm{Na}) - R(\mathrm{Mg}) &= 0.31, \\ \cdots\cdots\cdots & \\ R(\mathrm{O}) - R(\mathrm{F}) &= 0.10, \\ \cdots\cdots\cdots & \end{aligned} \qquad (12)$$

although in this case for anions and cations of different valences.

The difficulty pointed out above is general, since any comparison of interatomic anion–cation distances defines the true dimensions of ions only to within an arbitrary constant, which can be added simultaneously to all anionic radii and subtracted from all cationic radii (or conversely). Therefore it is not surprising that, together with the "classical" systems of ionic radii, there may exist also other systems, which differ sharply from the former. One of such "non-classical" systems was recently developed by Slater [51,52] on the basis of calculations of atomic wave functions [54,55] by the Hartree–Fock method and was tested on more than 1200 interatomic distances. This scale restores to a certain extent the system of Bragg radii [56], proposed before the beginning of the "ionic period" in crystal chemistry, and differs from the "classical" scale in that the radii of anions are reduced and those of the cations increased by 0.85 Å. It is remarkable that, although Slater's radii apply not to ions but to neutral atoms, nevertheless with their aid the experimental interatomic distances are satisfactorily reproduced even for crystals such as alkali metal halides.

Table 5. Experimental [52] (in brackets)* interatomic distances and the radii of singly charged ions in $A^{II}B^{VI}$ crystals

$R(B^{1-})$	B^{1-}	$R(A^{1+})$			
		1.35	1.65	1.82	2.01
		A^{1+}			
		Mg^+	Ca^+	Sr^+	Ba^+
0.75	O^-	2.10 * (2.10)	2.40 * (2.40)	2.57 * (2.57	2.76 * (2.76)
1.25	S^-	2.60 * (2.60)	2.90 (2.84)	3.07 (2.94)	3.26 (3.18)
1.38	Se^-	2.73 * (2.73)	3.03 (2.96)	3.20 (3.12)	3.39 (3.31)
1.40	Te^-	2.75 * (2.75) wurzite	3.05 (3.17)	3.22 (3.24)	3.41 (3.50)

* The upper number (without brackets) is the sum of ionic radii $R(A^+) + R(B^-)$. [53] The values denoted by an asterisk were used to calculate $R(A^+)$ and $R(B^-)$.

Another similar scale of ionic radii (corresponding to singly charged ions of the "divalent" elements Mg^+, Ca^+, ..., O^-, S^-, ...) was recently examined [53] in connection with the structure of the energy bands in crystals of compounds of the type $A^{II}B^{VI}$. These radii are listed in Table 5, which shows that they too give a good representation of interatomic distances, at least to within a reasonable accuracy of about 0.1 Å (see the footnote on p. 99).

2. Ionic Radii and Anion–Anion Distances

It may prove that the true dimensions of ions can still be derived from purely crystal-chemical data if, instead of anion–cation distances, one uses anion–anion distances and assumes that in certain structures anions can be in contact. Many years ago Lande postulated that such a case is realised in practice, for example in the structures of MgS and MnS and MgSe and MnSe, for which the interatomic distances are as follows (Å):

MgS	2.60	MnS	2.59
MgSe	2.73	MnSe	2.72 .

The approximate equality of the interatomic distances in the sulphides MgS and MnS and also in the selenides MgSe and MnSe enables Lande to assume [57] that the anions in these compounds touch one another and ultimately he obtained the following radii for the anions S^{2-} and Se^{2-}: $R(S^{2-}) = 1.83$ and $R(Se^{2-}) = 1.93$ Å.

However, even this treatment is in all probability incorrect, since the agreement between interatomic distances does not by itself constitute evidence that the anions touch—in any case anions with classical ionic radii. For example, the interatomic distances in binary compounds of the same structural type (NaCl) are [52]§ (Å):

Sm—O	2.49	Np—O	2.50
Pu—O	2.48	Pa—O	2.48
Ce—N	2.50	Gd—N	2.50
Np—N	2.45	Pu—N	2.45

and therefore agree with a precision which is not less than in the previous case. At the same time the O–O or N–N distance in these structures is approximately 3.50 Å, which in no way agrees with the sum of the "classical" ionic radii: $2R(O^{2-}) = 2.80$ Å and $2R(N^{3-}) = 3$ Å. Furthermore, together with such examples, it is not difficult to quote examples of the agreement between distances in structures with different anions and the same cations. For example, the interatomic distances (Å) [52]§ in certain binary compounds of zirconium, tantalum, uranium, and plutonium are

Zr—O	2.31	Zr—N	2.30
Ta—O	2.22	Ta—C	2.22
U—As	2.88	U—Se	2.88
Pu—N	2.45	Pu—C	2.46 ,

If these structures are examined from a purely crystal-chemical standpoint as was done by Lande, it would be logical to assume that the cations are in contact. However, one would then have to adopt for the ionic radii the values $R(Zr) = 1.63$, $R(Ta) = 1.56$, $R(U) = 2.03$, and $R(Pu) = 1.73$ Å, which are completely unacceptable from the standpoint of the "classical" scales (these values lead to the anionic radii $R(O) \simeq R(N) \simeq 0.6$–$0.7$ Å, $R(Se) \simeq 0.85$ Å, etc).

3. "Dimensions" of Ions

The ambiguous nature of any scale of ionic radii leads to the failure also of the second argument in favour of the ionic model. In fact it does not at all follow from experimental data that the "dimensions" of cations are much smaller than the "dimensions" of neutral atoms, while those of anions are much greater. Such a relation is typical only for "classical" scales. On the other hand, in Slater's scale [51,52] ionic radii are almost identical with atomic radii, and in the scale of Levin et al. [53] they differ only slightly from the atomic radii (Table 5). It is noteworthy that the greater anionic radii compared with those

§ Taken from R. W. G. Wyckoff's compilation "Crystal Structures", First Edition, New York, 1948 and checked by the authors against the Second Edition (New York, 1963).

of neutral atoms, required by the classical scale, are not confirmed by calculations of atomic wave functions [54,55]. On the contrary, for halide ions such calculations clearly indicate that the dimensions of the atoms remain unaltered when an electron is attached.

4. Limits of Stability

The Magnus–Goldschmidt limits of stability are usually quoted as the third crystal-chemical argument in favour of the ionic theory. For example, comparison of the O–O distances in the series MgO–CaO–SrO–BaO,

Compound	MgO	CaO	SrO	BaO
O–O distance, Å	2.96	3.40	3.64	3.90

shows that all crystals cannot be represented by close-packed spheres firmly in contact with one another. To explain this fact, it is assumed in classical crystal chemistry that close packing of anions corresponds to the minimum distance between oxygen atoms (in the MgO structure), which is 2.96 Å, and larger distances can be accounted for by the presence of gaps between the anions, which, however, satisfy the familiar "stability limits" [58] for the R(cation)/R(anion) ratio (Table 6).

Table 6. Magnus–Goldschmidt "stability limits" for various structures

Coordination number	Coordination polyhedron	R_A/R_B
2	line	0—0.155
3	triangle	0.155—0.225
4	tetrahedron	0.225—0.414
	square	0.414—0.732
6	octahedron	0.414—0.732
8	cube	0.732—1.000

It is readily seen, however, that these stability limits also cannot be regarded as a confirmation of the validity of the classical ionic radii for at least two reasons. The first is simply that, in fact, the classical ionic radii frequently do not satisfy the Magnus–Goldschmidt rules (Table 7). The second reason consists in the preconception (under the influence of the ionic theory) according to which "large" ions are necessarily assumed to be anions and "small" ions are taken to be the cations [52]. From the purely geometrical standpoint, there is no reason to reject the treatment of structures as close-packed cations (and not anions) [52], for which the stability limits would hold, as it were, "inversely". It is significant, however, that such a view has not merely a geometrical basis. If it is assumed that the negative charge of an atom cannot exceed unity [Sections (IV, 4) and (V, 2)], then we obtain in a natural manner a scale of the radii of singly charged ions of "divalent" elements, already mentioned in Section (III, 1). In this scale the structures of CaO, SrO, BaO, and to a smaller extent MgO consist of close-packed large metallic ions A^+, the octahedral vacancies of which contain the O^- anions, and the stability limits hold in many cases, albeit for the inverse ratio R(anion)/R(cation) (Table 8).

5. Other Methods for the Determination of Ionic Radii

Thus experimental data on interatomic distances do not yield convincing arguments either for or against the ionic theory, so that the classical scales of ionic radii must be regarded not as a basis but as a consequence of the ionic model. This conclusion applies also to other methods for the determination of ionic radii based on attempts to supplement or replace purely crystal-chemical data by other considerations. Such attempts were made at one time by Wasastjerne [42,43] and Pauling [47–49].

Table 7. Examples of the breakdown of the Magnus–Goldschmidt rule

Compound	Structural type	Coord. no., coord. polyhedron	$R(A^{2+})/R(B^{2-})$, (Pauling's radii), Å
BeO	wurtzite	4 tetrahedron	0.22
BeS	zinc blende	»	0.17
BeSe	ditto	»	0.16
BeTe	»	»	0.14
MgSe	NaCl	6 octahedron	0.33
SrO	NaCl	»	0.81
BaO	NaCl	»	0.97
PaO	NaCl	»	0.77
UP	NaCl	»	0.75
NpO	NaCl	»	0.79
PuO	NaCl	»	0.77
AmO	NaCl	»	0.77

Table 8. The ratios $R(B^-)/R(A^+)$ for various crystals

Crystal	Structural type	$R(B^-)/R(A^+)$	Crystal	Structural type	$R(B^-)/R(A^+)$
MgO	NaCl	0.55	FeO	NaCl	0.53
CaO	NaCl	0.45	CaO	NaCl	0.54
SrS	NaCl	0.69	NiO	NaCl	0.56
BaS	NaCl	0.60	CdO	NaCl	0.47
BaSe	NaCl	0.69	PaO	NaCl	0.43
BaTe	NaCl	0.70	UO	NaCl	0.44
TiO	NaCl	0.55	NpO	NaCl	0.43
VO	NaCl	0.58	PuO	NaCl	0.43
MnO	NaCl	0.51	AmO	NaCl	0.43

1. Wasastjerne based his treatment on experimental refractive indices and dielectric constants, assuming that the polarisability of ions α is proportional to their volume V, as for the primitive model of the atom considered as an ideally conducting sphere. Subdivision of the experimental distance (A–B) in the proportions $\sqrt[3]{\alpha_A} : \sqrt[3]{\alpha_B}$ is possible and yields a rough estimate of ionic radii; however, for this purpose it is necessary to divide in some way the overall polarisation of the crystal into increments corresponding to the individual ions. Wasastjerne determined the ionic radii assuming essentially that all polarised electrons belong to anions, but it is readily seen that the other hypothesis would lead to the opposite estimates.

2. Pauling's treatment [47–49], based on the postulate that in crystals the anions of the elements in Groups VII, VI, and V and the cation of the elements in Groups I, II, and III are isoelectronic, suffers from the same defect. Furthermore Pauling was forced to construct this scale of ionic radii in two stages. In the first stage he determined the so called "univalent" ionic radii R_1, assuming that the

corresponding anions are isoelectronic with ions of Group VII elements and that the ionic radius is inversely proportional to the Slater charge of external electrons:

$$R_1 = \frac{C}{Z_{\text{nucleus}} - Z_{\text{screen}}} \quad . \qquad (13)$$

However, the resulting interatomic distances differ appreciably from the experimental values (by about 0.5 Å). Therefore in the second stage Pauling modified the "univalent" ionic radii by introducing a correction for the hypothetical contraction of the ions in the crystal.

It is interesting that Pauling's equation (13) combined with the hypothesis that $A^{II}B^{VI}$ crystals contain only the singly charged ions $(A^{II})^+$ and $(B^{VI})^-$ yields satisfactory values for the interatomic distances also without this modification (Table 9). Then the radii obtained for the ions $(A^{II})^+$ and $(B^{VI})^-$ are found to be fairly close to the values obtained earlier [Section (III, 1), Tables 4 and 5].

Table 9. The ionic radii $R(A^+)$ and $R(B^-)$ and interatomic distances in $A^{II}B^{VI}$ crystals obtained by Pauling's equation (13). The experimental interatomic distances are given in brackets

$R(B^{1-})$	B^{VI}	$R(A^{1+})$			
		1,25	1,55	1,62	1,81
		A^{II}			
		Mg+	Ca+	Sr+	Ba+
0.88	O^{1-}	2.13 (2.10)	2.43 (2.40)	2.50 (2.57)	2.69 (2.76)
1.20	S^-	2.45 (2.60)	2.75 (2.84)	2.84 (2.94)	3.01 (3.18)
1.35	Se^-	2.70 (2.73)	2.90 (2.96)	2.97 (3.12)	3.16 (3.12)
1.55	Te^-	2.80 (2.75)	3.10 (3.17)	3.17 (3.24)	3.36 (3.50)

6. X-Ray Diffraction Data and the Ionic Model

The capacity of the atom to scatter X-rays (atomic scattering factor f_0) is roughly proportional to the number of electrons and therefore should be different for the neutral atom and the ion. Since the sublattices consisting of atoms bearing different charges are displaced relative to one another in the crystal structure, one may hope that the degree of ionisation will influence the details of the diffraction pattern. Attempts to test in this way whether or not the true charge distribution is consistent with the ionic model were frequently undertaken (see, for example, the literature review in Section IV in Urusov's thesis[59]) and one of the most typical of such attempts has been described by Raccah and Arnott[60]. Using three different values[61-63] of the atomic [form (Ed. of Translation)] factor for the doubly charged ion O^{2-} and the atomic [form] factor for the doubly charged ion Mg^{2+}, Raccah and Arnott showed that the divergence factor¶ in these three cases varies in the range 1.721–0.681%. For the two latest values[62,63] of the scattering factors of the O^{2-} ion, the R factor proved to be 0.849 and 0.881%. The results constitute at first sight convincing evidence in favour of the ionic model.

¶ The relative difference between the experimental and theoretical X-ray reflection intensities: $R = (\sum_{hkl} |I_E - I_T|)/(\sum_{hkl} I_E)$.

However, more detailed analysis shows that this conclusion is incorrect. In the first place the calculation of the intensities using the atomic factor for the singly charged ion[64] O^- in the same study led to $R = 1.326\%$, which falls precisely between the values of the R factor for the doubly charged ions (here one should also bear in mind that, while using the scattering factor for the singly charged O^- ion, the authors employed for magnesium the "doubly charged" atomic factor, as before).

Furthermore, there is yet another general consideration which makes any attempt to assess the degree of ionic character on the basis of X-ray diffraction data extremely risky. In any X-ray diffraction study the theoretical atomic scattering f_0 curve is always multiplied by a "temperature correction"

$$f_{\text{temp.}} = e^{-B(\sin\vartheta/\lambda)} \qquad (14)$$

(which has a characteristic value for atoms of each kind) taking into account the thermal vibrations of the atoms in the lattice (see, for example, Porai-Koshits[65]). The temperature corrections for each structure are found separately by an experimental procedure, which is in fact carried out precisely to ensure the minimum discrepancy between the intensities I_E and I_T. Since the atomic scattering factor is also fairly satisfactorily represented by the exponential function

$$f_0(\sin\vartheta/\lambda) \simeq (\text{no. of electrons}) \times e^{-A'(\sin\vartheta/\lambda)}, \qquad (15)$$

the resulting atomic temperature factor

$$f = f_0 f_{\text{temp.}} \simeq (\text{no. of electrons}) \times e^{-(A+B)(\sin\vartheta/\lambda)} \qquad (16)$$

may simulate the scattering factor for an ion of any charge type†.

IV. EFFECTIVE CHARGES AND THE COVALENT NATURE OF THE CHEMICAL BOND

We see that indirect (thermochemical and crystal-chemical) data cannot be regarded as an argument in favour of the ionic model. However, there also exist at present direct methods for the determination of effective charges of atoms in molecules and crystals. The data obtained with the aid of these methods in fact show that the chemical bond in inorganic crystals is significantly covalent‡.

1. Dipole Moments of Diatomic Molecules

The simplest method for estimating the effective charge lies in the measurement of the dipole moment. In a diatomic molecule A–B the effective charge (expressed as a

† A discrepancy may be observed only in the region of very low values of $\sin\theta/\lambda$ (see the plot in Freeman's paper[66]), particularly for amplitudes which are expressed as the differences between the atomic factors for the ions A and B. Such amplitudes are F_{111} for the NaCl lattice and F_{200} for the ZnS lattice. It is remarkable that an accurate estimate of the intensity of the I_{111} reflection for MgO yields an ionic charge $Z \simeq 1.2$–1.3.[59]

‡ Of course, in the assessment of the reliability of each effective charge obtained by a particular method, one must bear in mind that the concept of the effective charge of the atom in the molecule or crystal is itself to some extent arbitrary and only the values which are reproducible when obtained by different methods may be regarded as reliable [see Section (IV, 5)].

fraction of the electronic charge) can be defined by the relation

$$Z = \mu/4.8R, \qquad (17)$$

where the dipole moment μ is measured in debyes and the interatomic distance R in angstroms. The application of Eqn. (17) to the dipole moments of alkali metal halide molecules (in the gas phase) usually yields charges which are fairly close to $Z \simeq 1$. Recently the dipole moments of the diatomic molecules SrO and BaO were determined by microwave spectroscopy and were extrapolated to BeO (Table 10)[67]. Table 10 shows that the corresponding effective charges do not exceed unity, whereas according to the ionic model charges close to two would be expected in this case.

2. Dielectric Properties of the Crystal Lattice and Ionic Charges

The data in Table 10 do not permit the direct assessment of the effective charges in crystals for which the purely ionic state appears to be energetically the most favourable, since the Madelung constant for crystals is significantly greater than unity while the corresponding value for a diatomic molecule is unity. It is interesting, however, that the charges in Table 10 hardly change on transition to the crystal state. One of the most widely known methods for estimating effective charges in this case is based on the investigation of the dielectric properties of the crystal lattice.

Table 10. The dipole moments μ and effective atomic charges Z for certain molecules

Molecule	μ (D)	Z (e)
BeO	6.3	1.00
SrO	8.9	0.97
BaO	7.9	0.85

Szigetti[68] showed, in terms of the rigid and non-overlapping ion approximation, that the difference between the static (ϵ_0) and high-frequency (ϵ_∞) dielectric constants is related to the effective ionic charge Z by the equation

$$\varepsilon_0 - \varepsilon_\infty = \left(\frac{\varepsilon_\infty + 2}{3}\right)^2 \cdot \frac{4\pi Z^2}{\omega^2 V_m} \qquad (18)$$

where m is the reduced mass of the pair of ions A and B, V the volume per AB formula unit, and ω the frequency of the optical branch of lattice vibrations, which can be found by an independent method.

The effective charges "according to Szigetti"[68-78] are listed in Table 11, which shows fairly clearly the discrepancy with the value based on the concepts of the ionic theory.

The effective ionic charges can also be estimated using elastic and piezoelectric properties of crystals. The estimates obtained in this way, $Z_{BeO} \simeq 1$, $Z_{ZnO} \simeq 1$,[81] $Z_{ZnS} = 0.68$,[82] and $Z_{CdS} = 0.73$[83] or $\simeq 1$ [84] confirm the previous data.

3. Spin–Orbit Splitting

A method for estimating effective charges, which is significantly different from the preceding two, is based on the study of the spin–orbit splitting of levels in the valence band of crystals, which is reflected, for example, in a characteristic subdivision of peaks corresponding to interband transitions[85-87].

Table 11. Effective charges* "according to Szigetti"[68-89]

Crystal	Charge	Crystal	Charge	Crystal	Charge	Crystal	Charge
LiF	0.87[68]	RbI	0.89[68]	PbF_2	0.87[71]	BN	1.14[76]
NaF	0.93[68]	CsCl	0.84[68]	BeO	1.1 [72]	BP	0.25[76]
NaCl	0.74[68]	CsBr	0.79[68]	MgO	1.76[68]	InP	0.60[77]
NaBr	0.69[68]	TlCl	1.08[68]		1.20[79]		
				CaO	1.52[68]	GaAs	0.43[77]
NaI	0.71[68]	CuCl	1.10[68]		1.18[79]		
				SrO	1.16[68]	InAs	0.56[77]
KCl	0.80[68]	CuBr	0.995[68]		1.22[79]		
KBr	0.76[68]	CaF_2	0.74[68]	ZnO	1.06[73]	AlSb	0.48[77]
			0.83[69]	ZnS	0.96[68]	GaSb	0.30[77]
			0.82[70]		0.85[74]		
		SrF_2	0.65[68]				
			0.875[69]				
KI	0.69[68]		0.85[70]	CdS	1.00[74]	InSb	0.34[77,78]
		BaF_2	0.70[68]				
			0.90[69]				
RbCl	0.84[68]		0.86[70]	ZnSe	0.7[75]	Mg_2Si	0.6[80]
		CdF_2	0.79[71]				
RbBr	0.82[68]		0.82[70]	TiO_2	1.48[68]	Mg_2Ge	0.6[80]
						Mg_2Sn	0.6[80]

* For compounds A_2B and AB_2, the effective charge corresponds to the charge at the atom B.

From the standpoint of quantum mechanics, the effective charge of an atom corresponds to the probability p of finding a valence electron at this atom. Spin–orbit splitting is in fact a phenomenon in which the probability of observing the electron at oppositely charged atoms of the crystal is revealed in a fairly direct manner. As a result of the interaction of the spin and orbital momenta, the energy levels of the valence electrons in crystals split[86-88], and each atom makes its own contribution to the overall splitting, proportional to the probability of finding a valence electron at the atom. The resulting splitting Δ can thus be expressed in terms of the splittings for the individual atoms, Δ_A and Δ_B§, in the following form[88]:

$$\Delta \approx p_A \cdot \Delta_A + p_B \cdot \Delta_B, \; p_A + p_B = 1. \qquad (19)$$

All three splittings, Δ, Δ_A, and Δ_B, can be found by an independent method, so that Eqn. (19) makes it possible to determine from experimental data the required probabilities p_A and p_B or, conversely, to compare the experimental splitting Δ_E with the corresponding theoretical value Δ_T calculated with the aid of Eqn. (19) for this or a previously specified effective charge. The corresponding data are presented in Table 12. Comparison of this table

§ We may note that the quantities Δ_A and Δ_B for atoms in a crystal are not necessarily the same as the quantities Δ_A^0 and Δ_B^0 observed in the spectrum of the free atoms. Such agreement occurs at the point L of the valence band (for ZnS type crystals). In the centre of the Γ band $\Delta_A \simeq 3/2\Delta_A^0$ and $\Delta_B \simeq 3/2\Delta_B^0$.

with Table 11 shows that the charges "according to Szigetti", which are of the order of unity for $A^{II}B^{VI}$ compounds and of the order of 0.5 for $A^{III}B^{V}$ compounds, give rise to fully satisfactory agreement between the theoretical and experimental values of spin–orbit splitting.

Table 12. Spin–orbital splitting in crystals*

Crystal	AlAs	GaSb	InAs	InSb	ZnSe	ZnTe	CdSe	CdTe	HgSe	HgTe
Δ_E, eV	0.33	0.75	0.43	0.98	0.35	0.57	0.28	0.55	0.30	0.75
Δ_T, eV	0.33	0.76	0.41	0.89	—	—	—	—	—	—
$\Delta(B^-)$	—	—	—	—	0.29	0.65	0.29	0.65	0.29	0.65

* For the compounds $A^{III}B^{V}$, the splitting Δ refers to the centre of the zone and for the compounds $A^{II}B^{II}$ to point L. The effective charges used in the calculation of Δ_T for $A^{III}B^{V}$ were taken from Gielisse[76]. The data for the compounds AlAs–InSb were taken from Braunstein and Kane[89] and those for the compounds ZnSe–AgTe from Scouler and Wright[90].

4. X-Ray Spectroscopic Method for the Determination of the Effective Charge

The most direct and convincing evidence against the ionic theory comes, however, from X-ray spectroscopic data for molecules and crystals[91-93]. X-Rays are generated in transitions of outer electrons to inner atomic levels (X-ray emission spectra) and are absorbed in the reverse transitions (absorption spectra). Since the excess charge at the atom (positive or negative) leads to a displacement of the atomic energy levels, the study of the dependence of this displacement on the charge permits the experimental determination of the effective charges of ions in molecules and crystals by comparing their X-ray spectra with those of neutral atoms. The effective charges found by the X-ray spectroscopic method are listed in Table 13, three characteristic features of which are the most important: (1) the "X-ray spectroscopic" effective charges are usually in good agreement with the values estimated by other methods; (2) these charges are close in magnitude to the formal charges of the ionic theory mainly only for compounds of univalent elements; (3) whereas the charges of positive ions may reach fairly high values, those of negative ions do not exceed unity.

The data in Tables 11–13 show that this last property of effective charges is fairly general and is probably particularly important. Its importance is discussed below; here we may note that this feature is confirmed also by more detailed X-ray spectroscopic studies than the investigation of the displacement of the lines in the spectra. In a number of recent studies methods were developed whereby it is possible to assess the general structure of the energy levels and the form of the wave functions of the electrons in molecules and solids. A study of this kind on TiO, for example, showed[97] that the structure of the energy bands of this crystal is best interpreted on the basis of calculations[98] using singly-charged Ti^+ and O^- ions.

5. The Consistency of the Effective Charges and the Concept of the Effective Charge

The data on the effective charges obtained with the aid of the methods discussed above can be objected to on quite natural grounds, associated with the following factors: (1) the inaccuracy of the estimate of the effective charges by each method; (2) the incomplete consistency of different methods with one another; (3) the inadequacy of the concept of the effective charge itself. We shall examine these objections in order to obtain the answer to the question to what extent the effective charges estimated by various "direct" methods correspond to the "true" charges of ions in crystals and consequently to what extent such data really constitute evidence against the ionic theory.

Table 13. Effective charges Z found by the X-ray spectroscopic method*

Crystal	Z	Crystal	Z	Crystal	Z	Crystal	Z
NaF	0.58	MgS	1.05 −1.2	MnS	−0.86 −0.7 [95]	GaSb	0.33 [96]
NaCl	0.92	CaS	−1.1 −0.7 [95]	GeS	−0.71	InSb	0 [96]
NaBr	0.83	BaS	−0.71	SiO_2	1.97	Al_2O_3	1.53 1.77 [96]
NaI	0.75	ZnS	−0.86 −0.66 −0.3 [95]	SiS_2	1.69 −0.81	Al_2S_3	1.26 −1.00
MgF_2	1.30	CdS	−0.81 −1.5 [95]	$FeS_{1,98}$ marcasite	−0.96	Al_2Se_3	1.44
		$FeS_{1,093}$	−0.71 −0.7 [95]	CoS_2	−0.54	Al_2Te_3	1.44
$MgCl_2$	1.50						
$MgBr_2$	1.38	$FeS_{1.018}$	−0.96	NiS_2	−1.1	Mg_2C	0.34
Na_2S	0.75 −0.96	$CoS_{1,09}$	−0.61	MnS_2	−0.15	Li_2Si	−0.09
K_2S	−1.06	NiS	−0.66 −0.7 [95]	SnS_2	−0.54	Mg_2Si	−0.89
Ag_2S	−0.61	CuS	−0.51	AlN	1.32 1.17 [96]	Ca_2Si	−0.89
Cu_2S	−0.61	TiS	−0.61	AlP	0.87 0.87 [96]	Mg_2Sn	0.28
MgO	1.01 0.5 [94]	$TiS_{1.81}$	−0.81	AlSb	0.57 [96]		

* The minus sign denotes throughout the charges of the "electronegative" atom B (obtained from the displacement of the $K_{\alpha_{1,2}}$ doublet for this atom). All the charges, apart from those with individual references, were taken from Refs. 91 and 92.

1. The accuracy of each method may be checked by comparing the charges determined by the same method for different substances, in which the expected charges should have approximately the same value. Comparison of the charges determined, for example, by the method of Szigetti and by X-ray spectroscopic methods for the family of alkali metal halides or alkaline earth metal chalcogenides (Tables 11 and 13) shows that the results usually agree to within about $(0.1-0.3)e$ and therefore each method may be regarded as "accurate" within these limits. For the X-ray spectroscopic method, there exists yet another check, based on the possibility of an independent estimate of the charge at each of the atoms A and B in the binary compound AB. Experiment shows that both charges are usually found to be the same within the accuracy quoted above.

2. The consistency of the effective charges is clearly seen from a comparison of Tables 11–13 and also from Table 14 (taken from Urusov[59]), which lists about ten effective charges in ZnS obtained by a wide variety of methods. These tables show that the effective charges obtained by different methods are as a rule consistent to within the same limits, namely (0.1–0.3)*e*.

Table 14. Comparison of the effective charges in ZnS obtained by different methods

Charge	Method of estimation	References
0.96	Szigetti's method	68
0.85	infrared absorption spectra	74
0.68	measurement of piezoelectric constants	82
0.51	correlation with thermal ionisation of impurities	99
0.8	measurement of hyperfine splitting constant in ESR spectrum of impurity ions	100
0.86	X-Ray spectra	91, 92
0.66		
0.56	measurement of refractions	101
0.5	difference between optical and thermal width of the forbidden gap	102
0.7	study of magnetic susceptibility	103
Mean 0.7±0.2		

3. We shall finally examine the question of the validity of the concept of the effective charge itself, which is important for the understanding of the real significance of various experimental estimates. There is no doubt that the effective charge of an atom in a molecule or crystal is not a physical quantity with a completely valid definition, such as, for example, the mass of the atom or the charge of its nucleus. In fact, effective charges are used for an approximate representation of the real distribution of electron density. In various cases different approximations may be necessary, since, generally speaking, different "effective charges" correspond to different properties. Therefore any experimental method for the estimation of "effective charges" constitutes not only a method of measurement but at the same time also a method for the definition of the concept of the effective charge itself (this explains the discrepancies between the effective charges obtained by different methods). If the effective charges obtained by different methods showed a fairly wide scatter (from zero to the value of the formal valence), then the very concept of a "unique" charge attributable to the atom in the compound would of course lose significance.

However, experiment shows (see paragraph 2) that in fact all these values agree with one another within reasonable limits. Thus reference to the lack of validity of the concept of the effective charge would be justified only if it was possible to exclude altogether this concept from the theoretical scheme of quantum chemistry and the theory of the solid state (and this is scarcely possible at the present time). At any rate, the inaccuracy of this concept cannot serve as a basis for the return to the ionic theory, since the assertion that the charge, say, at the S atom in ZnS is nevertheless −2, already presupposes the use of some definition of the effective charge, for example one of the definitions which have been enumerated. However, experiment shows that *in the same sense* this charge can be much more correctly treated as close to unity.

V. THE PROBLEM OF MULTICHARGED NEGATIVE IONS FROM THE STANDPOINT OF QUANTUM MECHANICS

The small charge of negative ions is a general property of experimental effective charges, as already mentioned above. When Table 13 is examined, it is difficult to avoid the conclusion that it is precisely the impossibility of the attachment to the atom of more than one excess electron that constitutes the physical factor which "regulates" the distribution of charge in molecules and crystals. This conclusion is clearly illustrated in Table 15, which lists the effective charges at the oxygen atom in compounds with a wide variety of compositions and structures.

In this section an attempt is made to show that this conclusion not only follows from experimental data but probably is also a fairly natural consequence of simple theoretical considerations.

Table 15. Effective charges at the oxygen atom[91] in different compounds

Compound	Effective charge	Compound	Effective charge
MgO	1.01	Na_2SiO_3	1.14
SiO_2	0.99	$MgSiO_3$	0.98
Al_2O_3	1.02	$Al_2(SO_4)_3$	0.89
Na_2SO_4	1.09	$Mg(ClO_4)_2$	0.75
Na_3PO_4	1.15	$Al(ClO_4)_3$	0.73
$MgSO_4$	0.88	$Mg_3(PO_4)_2$	0.92
$AlPO_4$	0.94	$KAlSi_3O_8$	1.01

1. Localisation of the Electron and the Bound States

Table 16 lists the experimental values of the first two ionisation potentials and affinities for one electron for a number of "electronegative" atoms. Evidently the electron affinities of all the atoms (except halogens) are smaller approximately by a factor of ten than the ionisation potential, i.e. the binding energy of even one excess electron is always insignificant.

We shall consider this finding from the standpoint of quantum mechanics. The localisation of the electron at the atom (i.e. the presence of a "bound" state in the system electron–atomic residue is possible only when the potential well corresponding to the potential acting on this electron contains a "discrete spectrum" of energy levels¶.

It is known that in any field $U(r) < 0$ which vanishes at infinity, $\lim_{r\to\infty} U(r) = 0$, a discrete spectrum corresponds to negative energies, while a continuous spectrum corresponds to positive energies[104].

Thus Table 16 shows that the dissociation energy of an outer electron depends significantly on the effective charge

¶ The wave functions of a discrete spectrum decay at infinity according to an exponential law, so that the probability of finding an electron outside the atom is very small. On the other hand, the wave functions corresponding to a "continuous spectrum" decay to infinity very slowly. For example, in the case of a coulombic potential they have the asymptotic form[104] $Y_l^m(\theta, \varphi)(1/r)\sin(kr - \pi l/2)$ and decrease as $1/r$. Therefore in the state corresponding to the continuous spectrum the electron can be in no way localised at the atom.

and in the case of negative ions approaches the upper boundary of the discrete spectrum. If it is assumed that the effective charge can have fractional values (as is in fact the case in a molecule or a crystal), then, on the basis of the experimental dissociation energies for $Z = -1, 0, 1, 2, \ldots$, it is possible to plot an $E-Z$ interpolation curve showing the dependence of the energy of the outer electron on the charge at the atom. Curves of this kind for carbon, nitrogen, and oxygen are presented in Fig. 1. Evidently in all cases the $E-Z$ curve crosses from negative energy values to positive values at $Z \simeq -1$, i.e. the electron passes to a state corresponding to a continuous spectrum.

Table 16. Ionisation potentials[27] and electron affinities of various elements

Element	Electron-volts		
	I_2	I_1	F_1
F	34.98	17.42	3.45 [105]
Cl	23.80	13.01	3.61 [105]
Br	19.10	11.84	3.36 [105]
I	19.40	10.45	3.06 [105]
O	35.146	13.614	1.47 [106]
S	23.4	10.357	2.07 [107]
Se	21.5	9.75	1.7 [108]
Te	18.6	9.01	2.2 [108]
N	29.605	14.54	−0.1 [109]
P	19.65	11.0	0.7 [109]
As	20.10	9.87	0.6 [109]

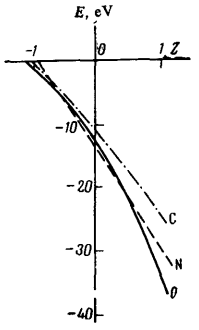


Figure 1.

In this connection one may point to the lack of physical significance of calculations of self-consistent wave functions for ions such as O^{2-}, N^{2-}, etc.[5,110,111] Indeed all such calculations start *a priori* with wave functions having an exponentially decaying radial component of the "Slater" type:

$$R(r) \propto ae^{-ar} \qquad (20)$$

(the parameters of this function are selected by a variational procedure), while functions of this type can be associated only with discrete spectra.

2. Localisation of the Electron in the Case of an Ion in the Lattice

Although Fig. 1 refers to isolated atoms and not to atoms in the lattice, one may assume that the presence of the lattice does not cause any significant change[113]. Fig. 2 presents a schematic curve for the potential U_0 of a given atom B_0 (for example oxygen) and the Madelung potential U_M acting on the electron assuming all the remaining lattice ions to be replaced by point charges. It is evident from Fig. 2 that in the region of B_0 the gradients of both potentials have opposite directions so that the Madelung potential of the lattice weakens rather than enhances the binding of the electron to "its" atom.

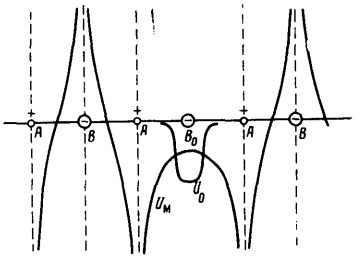


Figure 2.

This consideration can be made more general when account is taken of the fact that in the relevant range of effective charges, $Z_{B_0} \simeq -1$, the U_0 potential becomes of the short-range type and is simulated by a spherical potential well with a rectangular profile[29] (as for the short-range potential of nuclear forces). It is well known that the bound states (states corresponding to a discrete spectrum) in a well of this kind can exist only if the depth of the well u_0 is sufficiently great[104]:

$$u_0 \geqslant \frac{\pi^2\hbar^2}{8ma^2} \qquad (21)$$

(a is the radius of the well).

The experimental fact that the energies of all the outer electrons of all atoms become zero at $Z_{B_0} \simeq -1$ shows that with this effective charge the depth of the well u_0 becomes insufficient to retain the particle. However, it is evident that the Madelung potential U_M (Fig. 2) cannot make the well any deeper, since it reduces the level of its bottom at least to the same extent as it reduces the potential barrier between the atom B and the surrounding atoms A.

It follows from Eqn. (21) that the presence or absence of discrete spectrum levels in the spherical well is determined not only by its depth u_0 but also by its radius a. Therefore one might think that the effect of neighbouring atoms may increase not the depth but the width (radius) of the potential well. Calculation shows, however, that this effect is probably insignificant[112,113].

To make the treatment concrete, suppose that the radius of the well $a = 2$ a.u. $\simeq 1$ Å, i.e. about half the interatomic distance in typical oxides such as MgO. We shall now examine the relation between the depth of the well u_0 and the energy E of the lowest level in this well.

On solving the Schrödinger equation

$$\begin{aligned} &\frac{1}{r}\frac{d^2}{dr^2}(r\psi) + k^2\psi = 0, \quad k = \sqrt{2(u_0 - |E|)}, \quad r \leqslant a \\ &\frac{1}{r}\frac{d^2}{dr^2}(r\psi) - k^2\psi = 0, \quad k = \sqrt{2|E|}, \qquad\quad r > a \end{aligned} \qquad (22)$$

for this potential, it can be shown[104] that the energy of the lowest level is defined as the root of the transcendental equation

$$\sin ka = \pm \sqrt{\frac{1}{2a^2 u_0}} \qquad (23)$$

(the roots with $\cot ka < 0$ must be used[104]). The numerical solution of Eqn. (23) with $a = 2$ a.u. yields the curve relating $|E|$ to u_0 (Fig. 3), which can be more conveniently interpreted as the plot of the opposite function: $u_0 = u_0(|E|)$. We shall now make the reasonable assumption that, for each effective charge Z_B, the outer electron of the atom B is located at the lowest level E in the potential well due to the atomic skeleton and the remaining electrons. Then the dependence on Z of the quantity corresponding to the binding energy $|E|$ may be estimated from the plots in Fig. 1, and, on combining the plots in Figs. 1 and 3, it is easy to find also the relation $u_0 = u_0(Z_B)$. The dependence of the depth u_0 of the potential well on the effective charge of the oxygen atom,

$$u_0(Z) = u_0(|E|), \quad |E| = f(Z) \qquad (24)$$

is shown in Fig. 4. The experimental data allow this curve to be plotted only up to the point $Z = -1$. However, the probable extrapolation of this curve (dashed line) shows that at $Z \simeq -1.2$ the depth of the well u_0 becomes zero. Therefore, even if one assumes that the effect of the lattice can result in a decrease of the radius of the well, with the charge $Z \simeq -1.2$ the volume of the well nevertheless becomes zero and inequality (21) will not hold.

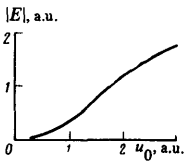


Figure 3.

It must be emphasised yet again that all the arguments adduced above refer only to negative ions. From the standpoint considered, positive ions, both in a free state and in a chemical compound, can have any charge, although excessively large positive charges are unlikely for other reasons. [Section (V, 4)]. Therefore the presence of singly charged ions, say, Ca^+ in CaO, does not contradict chemical facts requiring the presence of the doubly charged ion Ca^{2+}, for example the well known isomorphism of $NaNO_3$ and $CaCO_3$. If it is assumed that the Na atom in $NaNO_3$ indeed exists in the form of the Na^+ ion with a radius of 0.95 Å (which is also not entirely evident), then the similarity of the distances and the isomorphism of both compounds may be attributed to the presence of the doubly charged ions Ca^{2+} and CO_3^{2-} in $CaCO_3$. This leads, however, to an average negative charge at the oxygen atom (about 0.5). This illustrates the obvious fact that polyatomic anions can have charges greater than unity: −2, −3, −4 [for example in $Fe(CN)_6^{4-}$].

3. Other Causes of the Decrease of Ionic Character

The effect involving the "displacement" of the electron to a state corresponding to a continuous spectrum, mentioned above, thus constitutes the principal mechanism restricting the anionic charge to $|Z_{anion}| \simeq 1e$. However, from this point of view, $|Z| \simeq 1e$ must be regarded as only the upper limit of the possible charge. In fact the real charges in compounds can be still lower, due to energy considerations. This conclusion is apparently confirmed by experimental results (see Tables 11–13). In any of the compounds quoted in these tables the charge at the halogen atom may be unity. However, in no case does it actually reach this value. A similar conclusion follows from thermochemical and crystal-chemical arguments. Thus comparison of theoretical and experimental lattice energies of alkaline earth and transition metal halides[32] indicates a considerable departure from the ionic model.

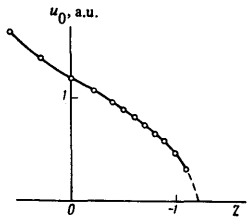


Figure 4.

Such departure from the purely ionic structure, with its characteristic tendency towards close packing, is indicated by much well known crystal-chemical data[58]. Thus, for example, BeF_2 has the open structure of cristobalite, while $BeCl_2$ forms a chain structure. $CaBr_2$ and $CaCl_2$ crystals have a deformed rutile structure with two Ca–Cl distances, namely 2.70 and 2.76 Å. In the $BaCl_2$, $BaBr_2$, BaI_2, $PbCl_2$, and $PbBr_2$ structures each metal atom is generally surrounded by nine halogen atoms at the vertices and at the centre of a trigonal prism, which in the case of $SrBr_2$ is also deformed. Calcium and lead iodides crystalise with the characteristic cadmium iodide layer structure. We may mention, finally, certain facts which suggest that even alkali metal halides are not completely ionic (Tables 11 and 13).

4. Description of the Nature of the Chemical Bond in Partially Covalent Crystals and the LCAO Method

We see that the crystals of inorganic compounds are to a large extent covalent and therefore in conclusion we shall consider the question of the description of the chemical bond in such crystals. The general postulates will be set out using as a typical example alkaline earth metal oxides[53], which makes it possible to demonstrate also how partial covalence can modify the physical properties of a solid.

The very concept of the chemical bond presupposes a definite approach to the theory of the electronic structure

of the molecules or crystals. The principal feature of this approach is that, within the framework of the theory of the chemical bond, we attempt to relate the electronic structure of the entire system to (a) the electronic structure of the constituent atoms of the system and (b) to the interaction of these atoms with one another. In the quantum chemistry of molecules principles (a) and (b) are expressed in the molecular orbital method, where one-electron functions of the entire molecule (molecular orbitals) are derived from the wave functions of the individual atoms (atomic orbitals). From the standpoint of the molecular orbital method, the chemical bond in an individual molecule of the MgO type is described, in the simplest variant, with the aid of a two-centre molecular orbital of the type

$$\psi = c_1\varphi_1 + c_2\varphi_2, \quad c_1^2 + c_2^2 = 1 \qquad (25)$$

$\varphi_1 = 2p_x$ orbital of O atom, $\varphi_2 = 3s$ orbital of Mg atom, where the relative values of the coefficients c_1 and c_2 determine the ionic character of the molecule.

In a coordination crystal of the MgO type individual molecules cannot be isolated. However, this is by no means necessary, since the molecular orbital method is in no way restricted to two-centre two-electron bonds. In this case it is most logical to treat the entire crystal as a giant "molecule" of $N \simeq 10^{24}$ atoms and to use the corresponding one-electron functions as the sum of the atomic orbitals of all the atoms constituting the crystal. This method, which is fully analogous to the LCAO-MO method in molecular theory, is well known in the physics of the solid state under the name "the strong bond method". Although each one-electron function (the so called "Bloch wave function") in the crystal contains a number of atomic orbitals of the order of 10^{24}, the actual application of the strong bond method is greatly simplified by the translational symmetry of the crystal lattice. As a result of the presence of translational symmetry, all the atomic orbitals φ, linked with one another by the translational motion of the lattice R, enter into the one-electron function of the crystal in the form of the combination

$$\psi = \frac{1}{\sqrt{N}} \Sigma_R e^{ikR} \varphi(r - R), \qquad (26)$$

where the summation is carried out over all the lattice sites. If each atom of the crystal has only one atomic orbital (and each unit cell contains only one atom), then Eqn. (26) will be the "true" one-electron function of the crystal (the eigenfunction of the effective one-electron Hamiltonian).

In a more complex case each "kind" of translationally non-equivalent atomic orbital has its own function of the type of Eqn. (26) and the overall one-electron function constitutes a linear combination of similar "basal" Bloch functions. For a crystal of the MgO type such basal Bloch functions are therefore the four functions formed from the $2p_x$, $2p_y$, and $2p_z$ orbitals of the oxygen atom and the ns functions of the metal atoms:

$$\begin{aligned}
\psi_1 &= (1/\sqrt{N}) \Sigma_R \exp(ikR)\, \varphi_1(r - R),\\
\psi_2 &= (1/\sqrt{N}) \Sigma_R \exp(ikR)\, \varphi_2(r - R),\\
\psi_3 &= (1/\sqrt{N}) \Sigma_R \exp(ikR)\, \varphi_3(r - R),\\
\psi_4 &= (1/\sqrt{N}) \Sigma_R \exp(ikR)\, \varphi_4(r - R),\\
\varphi_1 &= 2p_x,\ \varphi_2 = 2p_y,\ \varphi_3 = 2p_z,\ \varphi_4 = ns.
\end{aligned} \qquad (27)$$

Each overall Bloch function for the entire crystal will then constitute a linear combination of these four basal Bloch orbitals with certain coefficients c_1, c_2, c_3, and c_4:

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + e_4\psi_4, \ |c_1|^2 + |c_2|^2 + |c_3|^2 + |c_4|^2 = 1 . \qquad (28)$$

Fully by analogy with the LCAO-MO method for the MgO molecule, the coefficients c_1, c_2, c_3, and c_4 determine the ionic character of the crystal. Thus with $c_4 = 0$, the Bloch function (28) includes only the atomic functions of the anions. This case, like the case with $c_2 = 0$ in Eqn. (25), corresponds to a purely ionic state. With $c_4 \neq 0$, we have different degrees of covalence as a function of the relative value of the coefficient c_4.

We shall now consider briefly how covalence affects the physical (electrical) properties of the crystals, which depend on the structure of its energy levels.

In order to find the energy levels for the diatomic MgO molecules, it is necessary to set up the "secular" equation

$$\begin{vmatrix} \langle\varphi_1|\hat{H}|\varphi_1\rangle - \varepsilon & \langle\varphi_1|\hat{H}|\varphi_2\rangle \\ \langle\varphi_2|\hat{H}|\varphi_1\rangle & \langle\varphi_2|\hat{H}|\varphi_2\rangle - \varepsilon \end{vmatrix} = 0$$

two roots of which, ϵ_1 and ϵ_2, yield the required levels for the ground and first excited states. Quite analogously, in order to find the energy levels for the MgO crystal by the strong bond method, it is necessary to solve the following fourth-order "secular" equation:

$$Det|\langle\psi_i|\hat{H}|\psi_j\rangle - \varepsilon\delta_{ij}| = 0$$

with the basal Bloch functions (27). Since the latter depend on the vector k, each of the roots $\epsilon = \epsilon_i(k)$ also depends on this "wave vector". Ultimately we obtain 4 N different energy levels, which split into four individual "bands" or "zones": $\epsilon_1 = \epsilon_1(k)$, ..., $\epsilon_4 = \epsilon_4(k)$ (certain bands can of course overlap). In the case of the MgO type crystal under consideration the three bands with the smallest energy (partially overlapping) correspond to the 3 N occupied energy levels and form the so called "valence bands" (altogether in an MgO type crystal consisting of N formula units there are 6 N valence electrons, which occupy 3 N levels in pairs). The fourth band with $\epsilon = \epsilon_4(k)$ corresponds to unfilled, excited states. This is the conduction band and is separated from the valence bands by an energy "gap", called the forbidden gap. The width of the forbidden gap E_g is the most important electrophysical characteristic of the crystal and corresponds to the energy of the first optical transition in the molecule.

If the simplest possible approximation is used to calculate the structure of the energy bands, i.e. the treatment is restricted by (a) taking into account only the valence atomic orbitals and (b) taking into account only the interaction between anions and cations, then $E_g \simeq 11$, 9, 10, and 8.5 eV is obtained respectively for the series MgO–CaO–SrO–BaO.[53] These values are almost the same for the entire series, which is clearly inconsistent with experimental data, since in fact the width of the forbidden gap narrows from 8–9 eV[113,114] to about 4 eV[115] on going from MgO to BaO. It can be shown that, by taking into account the interactions between anions and the interaction of the 2s orbital of oxygen with the ns orbitals of the metal atoms, one cannot alter the variation of E_g in the series of oxides[53], so that the observed narrowing of the forbidden gap appears inexplicable at first sight. However, there is another important factor, which has a very pronounced effect on the width of the forbidden gap and which was not taken into account in the above estimate, namely, comparison of the metal–metal distances in oxides and in metals shows that the distances in the oxides are much shorter than in the pure metals. This fact by itself is not, of course, particularly important, since similar shortening is observed also in other compounds, for example in alkali metal halides. In the latter case, however, such decrease of the A^I–A^I distance does not at all suggest actual interaction

between the metal atoms, which are present in the crystal not in the form of neutral atoms but in the form of ions A^+. From the standpoint of the ionic theory, the oxides $A^{II}O$ constitute a fully analogous example. In all $A^{II}O$ crystals the quantity $2R(A^{2+}_{II})$ is smaller than the metal–metal distance and therefore, from the standpoint of the ionic theory, there is no real interaction between the A^{2+}_{II} ions. The situation is different if it is assumed that the $A^{II}O$ crystals contain only singly charged A^{+}_{II} ions. With the aid of the scale of singly charged ionic radii (see Table 5), it is easy to show that the quantity $2R(A^{+}_{II})$ is smaller than the metal–metal distance only for MgO and perhaps CaO. In SrO and particularly BaO real metal–metal interaction is to be expected and it is not difficult to show that even a very low value of the corresponding resonance integral leads to the required sharp narrowing of the forbidden gap[53].

Metal–metal interaction does not occur in purely ionic crystals and therefore it is to be expected that in the isoelectronic series of alkali metal halides NaF–KF–RbF–CsF a significant decrease of E_g should not be observed. Apparently experimental data[116] confirm this conclusion.

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Kurnakov Institute of General and
Inorganic Chemistry, USSR
Academy of Sciences, Moscow