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PHYSICAL PROPERTIES AND BOND TYPE IN Mg-Al OXIDES AND SILICATES

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ABSTRACT

From a study of physical properties that are sensitive to the electronic distribution, it is concluded that oxides and silicates of Mg and Al behave mostly as purely ionic compounds. Departures from ionic behavior are generally not such as to suggest covalent bonding.

INTRODUCTION

The solution of many petrological and geophysical problems demands an understanding of the nature of the interatomic forces in silicate minerals. The P-T range of stability of various phases, the kinetics of reactions between these phases, some of their magnetic properties, the velocity of propagation of elastic waves in the earth's mantle, its physical constitution, and its electrical conductivity, are examples of problems that involve some knowledge of the nature of interatomic forces in silicate minerals.

Of the various models that have been proposed for silicates, the ionic one, as developed by Goldschmidt, is by far the simplest. Once a set of ionic radii has been chosen, simple rules allow prediction of the coordination numbers and the general type of structure of a compound of given chemical composition. The interatomic attractive force is purely electrostatic, and the repulsive force, which arises from overlap of closed shells, contributes only a small fraction of the total lattice energy, so that its exact description is not essential to a first approximation and when dealing with phases at ordinary pressure. Goldschmidt's ionic model has unrivaled elegance and simplicity.

To be sure, not all elements and not all crystals obey the simple ionic rules. Attention has been called in recent years to an increasing number of substances for which the ionic model is inadequate (Fyfe, 1951, 1954; Goodenough and Loeb, 1954). Goldschmidt had, of course, noticed such discrepancies when he introduced into crystal chemistry the concepts of polarizability and polarizing power, both rather empirically defined. Polarization leads, in Goldschmidt's views, to a gradual transition to covalent bonding which will occur, according to him, when the polarizing power of the cations, as measured by their ionization potential, exceeds a critical value which depends on their charge and the polarizability of the anions. The present writer is not clear as to exactly what Goldschmidt's criteria may be for deciding that a compound is covalent rather than ionic; such criteria are indeed difficult to define.

An attempt to measure quantitatively the covalent character of bonds

was made by Pauling by means of his well-known electronegativity scale (Pauling, 1948a). The approach is again purely empirical. It leads to assigning to Si-O, Mg-O, and Al-O, bonds slightly more ionic character than Goldschmidt would grant. The most covalent of the three, according to Pauling, is the Si-O bond, with about 50% ionic character; Goldschmidt's chart (1954, p. 105) would make it purely covalent, although he mentions on the previous page that the "ionic character is about equal in strength to the covalent bonding." The actual charge distribution was later revised when Pauling (1948b) introduced his electroneutrality principle according to which "the electron distribution in stable molecules and crystals is such that the electrical charge associated with each atom is close to zero, in all cases less than ± 1 electron." The necessary redistribution of charge is effected by formation of π bonds, which lead to a contraction of the bond length. The calculation of the Si-O distance in $(SiO_4)^{4-}$ groups now becomes an intricate affair, involving essentially empirical corrections for 1) the Shomaker-Stevenson correction (for empirical electronegativity difference) to the sum of the covalent radii; 2) the (empirical) amount of π-bond character induced by the charge distribution; 3) the (empirical) bond contraction due to π-bond formation. How much simpler it is to note that the cosine of the tetrahedral angle (109°28′) being equal to $\frac{1}{3}$, the Si-O distance is $\sqrt{\frac{3}{8}}$ times the O-O distance; thus the conventional Goldschmidt oxygen-ion radius of 1.33 leads directly to an Si-O distance of 1.63!

The truth of the matter is that a complete and exact calculation, by quantum-mechanical means, of bond energy, lattice spacing, and elastic coefficients, of any structure more complicated than the hydrogen molecule still cannot be done. Approximations must be made, and empirical procedures resorted to. What is then the *simplest* model that will account best for most properties of the substance under consideration? Surely not the covalent one, as we still cannot compute an energy of covalent bonding (except by empirical means) for molecules more complex than H_2; no one has attempted, to the writer's best knowledge, to calculate from first principles the lattice energy of diamond. The pure ionic model no doubt is the simplest; and this paper is concerned mostly in finding how well an ionic model will account for a number of physical properties of silicates and oxides of magnesium and aluminum. Because of lack of experimental data on many of the more complex silicates (e.g. pyrope), this investigation deals mainly with the component oxides SiO_2, MgO, and Al_2O_3. The remarkable additive property of the entropies (Fyfe, Turner, and Verhoogen, in press) leaves little doubt, however, that the type of bonding in the more complex oxides and silicates is essentially the same as in the component oxides.

Some of the physical properties considered, such as the diamagnetic susceptibility and the electronic polarizability, depend critically on the average radius $\bar{r}$ of the electronic distribution, $\bar{r}=\int_0^\infty r\psi^2 dv$. To compute $\bar{r}$ (or $\overline{r^2}$, or $\overline{r^3}$, as the case may be) for an ionic structure, we consider here that all electrons occupy unperturbed orbitals of the ion to which they are assigned; all the electrons in O^{2-}, for instance, are assumed to occupy unperturbed orbitals $(1s)$, $(2s)$, $(2p)$, of the oxygen atom. For a covalent structure, on the other hand, we consider again pure atomic orbitals, neglecting the concentration of charge halfway between the atoms that would normally arise from covalent bonding. As will be seen, this approximation will in general appear to favor the covalent type; that is, if the ionic model appears more adequate than the covalent one computed on this approximation, it will *a fortiori* be more adequate than the exact covalent model.

The state of oxygen in the compounds we consider appears to be particularly critical, as the ionic structure of oxides and silicates requires the presence of a doubly charged O^{--} ion which is unknown in the free state, O^- plus one electron having a lower energy than O^{--}. O^{--} may, of course, be stabilized in ionic crystal by the additional coulomb energy that accrues from its greater charge, and a quantum mechanical calculation by Yamashita and Kojima (1952) indeed seems to confirm the existence of O^{--} in alkaline-earth oxides. Some of the testing methods used in this paper place special reliance on the electronic state of the anion, which is the main contributor to electronic polarizability and diamagnetic susceptibility. Such tests are thus particularly diagnostic of the state of the crystal as a whole.

Lattice Energies

As mentioned earlier, there is no way of calculating theoretically the lattice energy of a covalent compound. By contrast, the calculation for an ionic crystal may be carried out to a high degree of precision. The main term arises from the coulomb attraction between ions, which are assumed to have a spherically symmetrical charge distribution. Small corrections may be made for dipole-dipole and dipole-quadruple interaction, and for the zero-point energy, but the sum of these generally amounts to no more than a few per cent of the total. The main uncertainty arises from the repulsive potential, which may be evaluated either from compressibility measurements or from empirical considerations; again, the repulsive term is small, and the calculated value of the energy may be within 2 or 3% of the true value. A comparison with experimental values, which are probably not accurate to more than 4 or 5%, allows a check on the validity of the fundamental assumption regarding the ionic character of the substance.

A list of calculated and experimental values may be found in the Landolt-Bornstein Tables (1950), volume I, part 4, pp. 539–543. It appears from these lists, as is well known, that the agreement for the alkali halides, even CsI, is excellent; so is it for the oxides of the divalent elements and corundum. The diagnostic value of the method suffers, however, from the fact that the agreement is also quite good for sphalerite, wurtzite, galena, and other sulfides which one would hesitate, on other grounds, to call ionic. It is interesting that the lattice energy of substances that may not be purely ionic may apparently also be computed as if they were.

The following values (Table I), taken from the L.B. Tables, illustrate the general agreement for oxides.

TABLE I. LATTICE ENERGY
(Kcal/mole)

	Calculated	Experimental
BeO	1080	1053
MgO	936	913
CaO	830	823
Al_2O_3	3720	3609

CAUCHY RELATIONS

It is well known that if the lattice structure is such that every atom or ion occupies a center of symmetry, and if the particles interact with forces that depend only on distance (central forces), the following relations must exist among the elastic constants (Born and Huang, 1954, p. 136).

$$C_{23} = C_{44} \qquad C_{31} = C_{55} \qquad C_{12} = C_{61}$$
$$C_{14} = C_{56} \qquad C_{25} = C_{46} \qquad C_{36} = C_{45}$$

These relations are known as the Cauchy relations; they reduce the number of independent elastic constants in the general case from 21 to 15. In crystal with symmetry higher than triclinic, some of the Cauchy relations are identically satisfied, as the corresponding elastic constants are equal to zero. Thus, in hexagonal and rhombohedral crystals the Cauchy relations reduce to

$$C_{13} = C_{44}$$
$$C_{11} = 3\,C_{12}$$

regardless of whether there are, 5, 6, or 7 independent elastic constants. In cubic crystals, there is a single Cauchy relation

$$C_{12} = C_{44}$$

between the 3 independent elastic constants.

In crystals consisting of spherically symmetrical ions, forces should be central; in crystals held together by covalent bonds they should not. Thus the Cauchy relations could be used to test the ionic vs. covalent character of a compound, provided it fulfills the additional requirement that each particle should occupy a center of symmetry. This latter requirement rules out, for instance, corundum, but applies to any crystal with NaCl structure. NaCl itself, for which $C_{12}=1.30\ 10^{12}$ dynes/cm.^{2}, $C_{44}=1.278\times10^{12}$ dynes/cm.^{2} at 270° K. (Durand, 1936), seems indeed to satisfy the Cauchy relations; MgO, however, does not, as shown by the following figures (Durand, 1936).

T° K	C_{11}	C_{12}	C_{44}
		(10^{12} *dynes/cm.*^{2})	
80	29.87	8.56	15.673
300	28.93	8.77	15.477
560	27.25	8.96	15.092

Failures of the Cauchy relations in ionic crystals have been assigned to a number of causes. Herpin (1953) believes that they arise from the polarizability of the ions. Löwdin (1956) has shown by a thorough quantum-mechanical treatment of the alkali halides that a notable fraction of the lattice energy arises from many-body potentials. The forces acting between two ions depend on the presence or absence of other ions in the neighborhood, and are therefore not purely central, i.e., function of only the separation between the ions. Laval (1957) and his collaborators have insisted that the introduction of non-central forces must, in fact, invalidate the classical theory of the elasticity of crystals; there should be, in the general case of non-central forces in a triclinic crystal, 45 rather than 21 independent static elastic constants.

Whatever the case may be, it should be noted that very few substances, if any, satisfy the Cauchy relations. The agreement for NaCl mentioned above is really fortuitous, as the temperature coefficients of C_{12} and C_{44} have opposite signs (see Hearmon, 1956). Thus the Cauchy relations offer no test of whether a crystal is ionic or not; what they test is whether the ions are deformable or not. In addition, Löwdin has shown quantitatively for NaCl that the difference between C_{12} and C_{44} arises almost entirely from the repulsive term in the expression for the potential energy of the crystal; this repulsive term, in turn, is only a fraction of the total energy. Thus the existence of many-body potentials will only slightly affect the cohesive energy, which, as we know, comes out correctly on the ionic hypothesis. Stated in other words, elastic constants being second derivatives of the potential energy, one might obtain a potential energy function which would not yield the correct elastic constants but which would still give usable results with regard to the cohesive energy and the volume.

X-RAY METHODS

If one now looks for physical properties that depend on the actual distribution of electrons in the crystal, the atomic scattering factor f first comes to mind. This factor, which is the ratio of the radiation amplitude scattered by the charge distribution in an actual atom to the amplitude scattered by a point electron at the center, is

$$f = \int_0^\infty U(r) \frac{\sin \mu r}{\mu r} dr$$

where $U(r)$ is the radial electronic density and $\mu = 4\pi \sin\theta/\lambda$, λ being the wave length of the radiation, and θ the angle between the direction of the incident radiation and the scattering plane. One notes that for $\theta = 0$, $f = Z$, the total number of electrons in the atom. Thus, if one could

TABLE II. ATOMIC SCATTERING FACTOR OF ALUMINUM AND ALUMINUM IONS*

	Sin $\theta/\lambda \times 10^{-8}$			
	0.0	0.1	0.2	0.3
Al^{3+}	10.0	9.7	8.9	7.8
Al^{2+}	11.0	10.3	9.0	7.75
Al^{+}	12.0	10.9	9.0	7.75
Al	13.0	11.0	8.95	7.75

* Hartree, with interpolation for Al^{+} by James and Brindley. L. B. Tables, vol. I, part 1, p. 300.

measure f for various values of θ at fixed λ, extrapolation of the experimental curve to $\theta = 0$ would indicate whether the atom is ionized, and to what degree. Atomic scattering factors have been calculated for many atoms and ions from the charge distribution computed by various methods (Hartree's self-consistent field, Thomas-Fermi, etc.); these calculations generally show that the scattering factors for an atom and the corresponding ions differ appreciably only at small values of μ, as shown in Table II for aluminum.

The Landolt-Bornstein Tables (vol. I, part 1, pp. 300–310, 1950) give an extensive list of references on the experimental values of scattering factors; these may then be compared with theoretical values to determine the actual charge on the atom. The experimental determinations require that due allowance be made for thermal vibrations, which depend on the temperature and the compound of the atom being studied. Various other necessary corrections, as for extinction, were not made in early work. We note the value of f for oxygen in Fe_3O_4 at $\sin\theta/\lambda = 0.07$, which is 9.3 (Claasen, 1926); this implies a negative charge greater than that of

O^{-}, for which $f=9.0$ at $\theta=O$. Froman (1930) found the total number of electrons on oxygen in MgO to be 9.3, the corresponding number for Mg in the same substance being 10.32. Wyckoff and Armstrong (1930) also determined the scattering factors for oxygen and magnesium in MgO, but only for values of sin θ/λ which do not allow a discrimination between the various possible electronic states. For the values for MgO determined by Brill, Hermann, and Peters, see below.

Essentially the same information that goes into the determination of the scattering factor may be used for a Fourier analysis, which gives in a more graphic form a representation of the electron density distribution in a crystal. By integration of the density outward from an atomic position to a radius where the electronic density is negligible, the total charge on an ion in the crystal may be computed. Several investigators, using this method, agree that the total charge on Na in NaCl is close to 10.05 electrons, that on Cl being about 17.85 (Witte, 1956; Brill, 1939; Havighurst, 1927); this corresponds to about 90% ionic character, which is considerably more than the Pauling electronegativity scale would allow. Brill *et al.* (1939) find a density of only 0.006 electrons/Å^3 at positions ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$). Brill, Hermann, and Peters (1948) have also examined MgO; they find a distribution that is less localized than in NaCl, the density in MgO nowhere being less than 0.15–0.2 electrons/Å^3. There is, however, no indication of directional bonding: the density at the same distance is about the same in the [100] and [110] directions. This is in contrast with diamond, in which there is a strong charge concentration on lines joining the atoms, with corresponding low electronic densities at other points. The atomic scattering factors, corrected for temperature, are listed in Table III, together with the theoretical factors from the Hartree-James-Brindley Tables.

The experimental scattering factors listed in Table III are not inconsistent with a purely ionic structure. Brill, Hermann, and Peters (1948) concluded, however, from a more detailed study of the electronic density distribution, that a certain amount of covalent bonding must be present. The density distribution is indeed interesting: going out from an atomic position the density at first drops sharply in all directions, then tails off to a fairly uniform value. This occurs at about 0.9 Å from the center of a magnesium position along the [111] and [110] directions, and at about 1.15 Å from the center of the oxygen position along these same directions. Only in the [100] direction is there a sharp minimum (0.3e/Å^3) at about 1.0 Å from Mg and 1.1 Å from O. The ions thus both seem to be very nearly spherical, although magnesium seems larger, and oxygen smaller, than their conventional ionic radii would predict. Along the [111] direction one finds a zone, about 1.6 Å in length, along which the density has an almost constant value of 0.15–0.20e/Å^3.

TABLE III. EXPERIMENTAL SCATTERING FACTORS IN MgO,* AND THEORETICAL VALUES†

Sin θ/λ	Mg exp.	Mg^{++}	Mg	O exp.	O^{--}	O^{-}	O
0	—	10.0	12.0	—	10.0	9.0	8.0
0.1	(9.5)	9.75	10.5	(8.0)	8.0	7.75	7.1
0.2	8.24	8.6	8.6	5.76	5.5	5.65	5.3
0.3	7.06	7.25	7.25	4.02	3.8	3.95	3.9
0.4	5.78	5.95	5.95	2.87	2.7	3.0	2.9
0.5	4.65	4.8	4.8	2.25	2.1	2.3	2.2
1.0	2.02	2.0	2.0	1.36	1.35	1.35	1.35

* Brill, Hermann, and Peters, 1948.

† L. B. Tables, vol. I, part 1, p. 300. Values for Mg^{++} and O do not agree well with recent calculations by Berghuis *et al.* (1955).

In Table IV are listed some electronic densities computed either from the approximate Slater wave functions (see for instance Coulson, 1952, p. 40) or, when available, from the density distribution curves in the Landolt-Bornstein Tables, vol. I, part 1, pp. 284 ff.; the latter curves are plotted from a variety of sources, most of which use the method of Hartree's self-consistent field.

The last entry in the table is the computed density midway between oxygen and magnesium, assuming a double covalent bond of the type $\psi=\psi_0(2p_x)+\psi_{Mg}(3s)$, the bond length being taken as 2.1 Å. The $(2s)$ and $(2p)$ orbitals of Mg, and the $(2s)$ and remaining $(2p)$ orbitals of oxygen are assumed to be undisturbed.

The observed density of 0.3 between Mg and O along the cube edge is seen from Table IV to be consistent with a superposition of the densities of Mg^{++} and O^{--}; it is much less than the covalent value 0.63. The den-

TABLE IV. TYPICAL ELECTRONIC DENSITIES

Atom or ion	Distance from center of atom (Angstrom units)	Electronic density (electrons/Å^3)	Source
Mg^{++}	0.85	0.13	L.B. Tables
O	1.06	0.16	L.B. Tables
	1.27	0.06	L.B. Tables
	1.9	<0.004	L.B. Tables
O^{-}	1.06	0.2	L.B. Tables
	1.27	0.09	L.B. Tables
	1.9	0.008	L.B. Tables
O^{--}	1.06	0.27	Calculated from Slater function
	1.85	0.002	Calculated from Slater function
Mg–O covalent	1.05	0.63	See below

sity of about 0.2 at 1.15 Å from oxygen along the face and body diagonals is again about correct for an undisturbed O^{--} ion, but the diffuse and even distribution between ions of opposite sign along the body diagonal, and between ions of the same sign along the face diagonal, cannot be reconciled with a simple ionic model nor, for that matter, with any simple covalent model. As Brill, Hermann, and Peters point out, the situation is somewhat reminiscent of the distribution in metals. The total number of electrons on Mg and O, out to a given distance, is given in Table VII.

Too much weight should not be given to these figures, as they must embody the fundamental uncertainties inherent in the type of analysis: clearly, one cannot expect much detail or precision on the scale of 0.1 Å when using radiation with a wave length many times larger. One derives, however, the rather surprising result that in MgO the net charge on Mg is probably somewhat larger than 2, while that on O is somewhat less than 2. The structure is thus not a simple ionic one, but deviations are not of the type expected in covalent bonding. In particular, the spherically symmetrical distribution of charge around the nuclei, the absence of any localized bonds such as found in diamond, and the appreciable, but smooth and uniform electron density over a large fraction of the cell suggest more a transition to a metallic state than to a covalent one.

To the writer's best knowledge, no detailed studies of this kind have been made on any other oxide of the element under consideration. One notes with interest that Parker and Whitehouse (1932) found a full complement of 26 electrons on Fe in pyrite (FeS_2), and that Witte (1956) finds indications of electron concentration between Li and F in LiF, making this substance somewhat less ionic than NaCl.

Diamagnetic Susceptibility

An electron moving within an atom is equivalent to a tiny current in a resistanceless conductor. When an external magnetic field is applied through an electrical circuit, an induced current is set up, the magnetic effects of which tend to oppose the primary field. In the same way the electronic motion within an atom will be disturbed by an applied magnetic field in a way such as would be equivalent to a current tending to cancel the applied field. This effect leads to diamagnetism, which exists in all substances, although it may be overshadowed by more powerful effects of the opposite sign in paramagnetic or ferromagnetic materials. It can be shown (e.g., Kittel, 1953, pp. 134–135; Selwood, 1956, chap. V) that the diamagnetic susceptibility for unit volume χ_v is given by the simple Langevin expression

$$\chi_v = -\frac{Ze^2N}{6mc^2}\overline{r^2} \qquad (1)$$

where N is the number of atoms per unit volume, Z the number of electrons per atom, e and m, respectively, the charge and mass of the electron, c the velocity of light, and $\overline{r^2}$ is the mean square distance of an electron from the center of the atom. Instead of χ_v one also uses the molar susceptibility χ_M, which is equal to χV, V being the molar volume, and the specific susceptibility, or susceptibility for unit mass, $\chi_d = \chi_M / M$, M being the molecular weight. Substituting numerical values of fundamental constants in (1), one finds

$$\chi_M = -2.82\ 10^{10} \sum \overline{r^2}$$

where the summation is to be extended over all the electrons in each atom. If radial distances are expressed in atomic units ($a_0 = 0.528 \times 10^{-8}$ cm.), we get

$$\chi_M = -0.79\ 10^{-6} \sum \overline{r^2}.$$

Thus the diamagnetic susceptibility depends essentially on the radial distribution of electrons around the nuclei, which would be different in covalent and ionic structures. If one compares, for instance, the structures Mg-O and Mg^{++}-O^{--}, the 2 electrons transferred from Mg to O will occupy on the oxygen ion orbitals of smaller average radius than that of the ($3s$) electrons of the isolated magnesium atom. As the effect of a covalent bond is generally to concentrate charges between the bound atoms, the change from the covalent to the ionic structure should be accompanied by a notable decrease in susceptibility. A comparison of calculated and observed values of χ will thus give information regarding the actual state in the crystal. One notes that, in general, the larger anions will contribute more to the susceptibility than the smaller cations.

Formula (1) is strictly valid only if the charge distribution is spherically symmetrical. For diatomic and other non-symmetrical molecules, one must add a term of opposite sign which represents a paramagnetic contribution (Van Vleck paramagnetism) differing from ordinary paramagnetism due to uncompensated spins in that it is temperature independent. Theoretically the Van Vleck term should vanish only in completely symmetrical systems in which the field direction is an axis of symmetry and the electronic distribution is spherically symmetrical about the nuclei; it is difficult to evaluate exactly and is not likely to be important in crystals of high symmetry.

For an electron with wave function ψ, it follows from the definition of $\overline{r^2}$ that

$$\overline{r^2} = \int_0^\infty r^2 \psi^2 dv$$

and may therefore be calculated if the wave function ψ is known. A particularly simple formula can be obtained for $\overline{r^2}$ if one uses Slater wave

functions of the type

$$\psi = Ar^{n-1}e^{-cr/n}$$

where A is a normalizing factor, n is the principal quantum number of the electron, and c, the effective charge, is equal to the atomic number Z minus the screening constant s which is computed according to Slater's well-known rules (see, for instance, Slater, 1951, p. 476). A simple integration yields directly

$$\overline{r^2} = n^2(n + \tfrac{1}{2})(n + 1)/c^2. \tag{2}$$

Pauling (1927), by a more elaborate calculation, finds

$$\chi = -2.01 \times 10^{-6} \sum \frac{n^4}{(Z - s)^2}\left[1 - \frac{3l(l + 1) - 1}{5n^2}\right] \tag{3}$$

where l is the second quantum number of the electron. Pauling gives in tabulated form the susceptibilities of many common ions. For O^{--}, for instance, he finds $\chi_M = -12.6 \times 10^{-6}$, whereas the simpler Slater formula (2) gives -12.8×10^{-6}. Susceptibilities have also been calculated from various other models and are collected in the Landolt-Bornstein Tables (vol. I, part 1, pp. 394 ff.). A calculation using the Thomas-Fermi-Dirac model has recently been made by Thomas and Umeda (1956).

Experimental susceptibilities of ions have been obtained from measurements on solutions and crystals. It appears that ionic susceptibilities are nearly additive; for example, the difference between the molar susceptibilities of LiF and NaF is nearly the same as the difference between LiCl and NaCl. The matter is reviewed by Selwood (1956), who gives (p. 78) an extensive table of ionic susceptibilities.

The diamagnetic susceptibility of minerals is difficult to measure, because of paramagnetic impurities (e.g., Fe^{++} or Fe^{+++}) which may overshadow the diamagnetic effects, even when these impurities are present only in very small amounts. Surprisingly, there is even some uncertainty regarding the susceptibility of common oxides. Yamashita and Kojima (1952), while studying the electronic state of O^{--} in MgO, used a value of -18.8×10^{-6} for the molar susceptibility of this oxide; there are, however, several other determinations which give an average value of -10.5×10^{-6} (Ray, 1955). The International Critical Tables (vol 6) gives on page 359 a value of -10.2 (in units of 10^{-6}) for Al_2O_3, and on page 364 a value of -34.7; the latter value will be used here, as it agrees with measurements of Rao and Leela (1953) on white sapphire. Corundum is slightly anisotropic, and the value given here is an average. Spinel ($MgAl_2O_4$) is listed in I.C.T. as paramagnetic ($\chi_M = +88 \times 10^{-6}$) which seems unlikely in the absence of iron or manganese impurities.

The following table (Table V) shows the molar diamagnetic suscepti-

TABLE V. MOLAR DIAMAGNETIC SUSCEPTIBILITIES (IN UNITS OF -1×10^6)

	O	O^{--}	Mg	Mg^{++}	Al	Al^{3+}	Si	Si^{4+}	C^{4+}	C	C^{4-}
Pauling	—	12.6	—	3.2	—	2.5	—	2.1	0.15	—	50.0
Slater	7.0	12.8	27.5	3.1	26.9	2.5	25	2.0	—	7.4	—

bility of several ions and atoms computed by Pauling (1927) or by Slater's formula (2).

From these values one obtains by simple addition the following values (all multiplied by -1×10^6), which may be compared with listed experimental values (Table VI).

The figures for diamond show that the diamagnetic susceptibility of a covalent crystal is not very different from that computed by addition of atomic susceptibilities; we note that the susceptibility per atom of diamond is greater than that of a single carbon atom, in keeping with the expected effect of covalent bonding mentioned above. By contrast, the figures suggest a truly ionic state for SiO_2. For Al_2O_3 the agreement between the experimental susceptibility and the sum of the susceptibilities of the ions is still fairly good; clearly, the state of Al_2O_3 is more ionic than covalent. The figures for MgO require closer scrutiny.

Yamashita and Kojima (1952) have examined the stability of the O^{--} ion in oxide crystals. Using Hartree-Fock wave functions for Mg^{++} and (1s) and (2s) electrons of O^{--}, they determine by a variational method the parameters of an empirical wave equation for (2p) electrons that will minimize the energy of the crystal for an Mg-O distance of 2.1 Å. Repeating the procedure for O^-, they find that O^{--} is decidedly more stable (by about 12 e.v.) than O^- in magnesium oxide. They also compute the ionic susceptibilities which they find to be -3.7×10^{-6} for Mg^{++} and -21.0×10^{-6} for O^{--}, in this same compound. This would make the molar susceptibility of MgO (-24.7×10^{-6}) much too large in absolute value.

Essentially the same result would accrue from the electron density distribution of Brill, Hermann, and Peters discussed above. It will be recalled that the main features of this distribution are: 1) an unusually

TABLE VI. CALCULATED AND EXPERIMENTAL* SUSCEPTIBILITIES, FOR VARIOUS STRUCTURES (IN UNITS OF -1×10^{-6})

MgO			Al_2O_3			SiO_2			C (diamond)		
Mg–O	Mg^{++}–O^{--}	exp.	Al–O	Al^{3+}–O^{--}	exp.	Si–O	Si^{4+}–O^{--}	exp.	C–C	C^{4+}–C^{4-}	exp.
34.5	15.9	10.5	74.8	43.55	34	39	27.6	25.6	14.8	50.15	12.0

* Value for MgO from Ray (1955); others from International Critical Tables.

large magnesium ion, extending outward to 0.9-1 Å; 2) a very high and uniform density between the oxygen and magnesium; this density being almost as large as that (0.3 electron/A^3) of the conduction electrons in Al (Witte, 1956); and 3) a somewhat small oxygen ion. If the diffuse charge is assigned to any one of the ions, its spatial extension becomes so large that its diamagnetic susceptibility, which is proportional to $\overline{r^2}$, becomes enormously greater than the experimental value.

The following table (Table VII) gives the total number of electrons and the corresponding ionic susceptibilities computed by integration of the density data of Brill, et al., out to a specified distance. From this table we see that if we assume, for instance, radii of 0.9 for Mg and 1.2 for

TABLE VII

Mg			O		
1 Radius (Å)	2 Total number of electrons	3 Diamagnetic susceptibility	4 Radius	5 Total number of electrons	6 Diamagnetic susceptibility
0.9	9.2	5.8	1.15	8.3	9.0
1.0	9.6	6.9	1.20	8.6	9.7
			1.33	9.0	10.9
			1.40	9.3	11.9

oxygen, the total number of electrons on the ions is $9.2+8.6=17.8$, leaving 2.2 electrons per ion pair in the inter-ionic space; the sum of the susceptibilities of Mg and O comes out as 15.5, which again is more than the experimental value. From this we infer that a small paramagnetic susceptibility must also be present. This paramagnetic contribution is considerably smaller than the Pauli paramagnetism of interstitial electrons with a density of 0.2/Å^3; these should anyhow form a filled band and could not be regarded as "free," as the extremely low intrinsic conductivity of MgO clearly shows. Similarly, the paramagnetism due to a single uncompensated electron spin, as would occur in ions such as O^- or Mg^+, would be of the order of 10^{-3} rather than 10^{-6} at ordinary temperature. Thus presumably the small paramagnetic contribution must be a Van Vleck term, arising from the fact that the field at the center of the cube forming $\frac{1}{8}$ of the unit cell is far from symmetrical; indeed, on any body diagonal of this elementary cube there are ions of *opposite* signs on either side of the side.

Summing up, the diamagnetic susceptibility of SiO_2 is consistent with that calculated for a purely ionic structure. The agreement between measured and calculated values for an ionic model of Al_2O_3 is not very

good, and it is bad for MgO. In the latter compound, there is probably a small paramagnetic component arising from a high electronic density in regions of the unit cell where the field is not centro-symmetric. Departures between measured and "ionic" susceptibilities are definitely not suggestive of covalent bonding, the ionic values being intermediate between experimental and covalent ones.

Polarizability

When a dielectric substance ("insulator") is subjected to an electrical field E, charges within the substance may be displaced. Now displacing a charge $+e$ by a distance x is equivalent to adding a charge $(-e)$ at the original position and a charge $+e$ at the new position; this, in effect, is equivalent to adding a dipole ex in the direction of the displacement. If the polarization P is defined as the vector sum of the induced dipoles per unit volume, the displacement vector D is defined as $D=E+4\pi P$, and the dielectric constant ϵ, which is the ratio of D to E, is given by the relation

$$\epsilon = 1 + 4\pi \frac{P}{E} = 1 + 4\pi\kappa \tag{4}$$

where $\kappa = P/E$ is the electrical susceptibility.

Consider an atom of type i in a crystal, and assume that under the effect of the electrical field E_{loc} acting on it, it acquires a dipole moment p_i. The polarizability α_i of this atom is then defined as $\alpha_i = p_i/E_{\text{loc}}$ and

$$P = \sum_i E_{\text{loc}} N_i \alpha_i \tag{5}$$

where N_i is the number of atoms of type i per unit volume. If one further defines $\alpha = \sum_i n_i \alpha_i$, where n_i is the number of atoms i per molecule, one may write

$$P = N \frac{\alpha}{V} E_{\text{loc}} \tag{6}$$

where V is the molar volume and N is Avogadro's number.

E_{loc} is the effective field acting on an atom inside the solid. If one sets simply $E_{\text{loc}} = E$, one gets the well-known Drude formula

$$\epsilon - 1 = 4\pi \frac{N}{V} \alpha.$$

In general, however, the field at any point inside the crystal is the sum of the external field E and contributions arising from the polarization of neighboring atoms. The calculation of E_{loc} is complicated, except in cases where the distribution of atoms is isotropic, or where the lattice

has a high degree of symmetry* (see Kittel, p. 92). One finds then

$$E_{\text{loc}} = E + \frac{4}{3}\pi P \tag{8}$$

from which derives the well-known Clausius-Mosotti formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi \frac{N}{V}\alpha. \tag{9}$$

A more general expression used by Mott and Gurney is

$$E_{\text{loc}} = E + \frac{4}{3}\pi\gamma P \tag{10}$$

where γ is an empirical factor to be determined from experiments.

We must now consider two separate effects. When the field has a very high frequency, as in the visible part of the spectrum, the dielectric constant in media of unit magnetic permeability is equal to the square of the index of refraction; accordingly, from (9) we get

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3}\pi \frac{N}{V}\alpha \tag{11}$$

a relation known as the Lorentz-Lorenz equation from which α may be determined. This value of α is called the "optical," or "electronic" polarizability, as the polarization arises entirely from shifts in the distribution of the electron clouds with respect to the positively charged nuclei. At lower frequencies, as in the infrared, an additional effect arises from the relative displacement of the positive and negative ions in the crystal. This additional contribution to the dielectric constant is said to arise from "atomic" or "ionic" polarizability. In purely covalent crystals, such as diamond, there is no ionic polarizability, as the atoms carry no net charge; accordingly their dielectric constant in low-frequency or static fields is equal to the square of the index of refraction corrected for dispersion. A comparison of the index of refraction, suitably extrapolated to zero frequency, with the dielectric constant in static fields affords thus a measure of the ionic character of the substance.

We consider first the electronic polarizability.

Electronic Polarizability

From (11) it follows that α has the dimensions of a volume; indeed one would expect the deformability of an atom to be proportional to its spatial extension. A theoretical calculation of the polarizability is easy

* More precisely, the condition is that the coordinates $x_i y_i z_i$ of the lattice points around a central lattice point taken as the origin should satisfy the condition that $\sum(r_i^2) = 3\sum(z_i^2)$, where $r_i^2 = x_i^2 + y_i^2 + z_i^2$. This condition is satisfied if $x_i^2 = y_i^2 = z_i^2$.

for simple atoms, such as hydrogen: all that has to be done is to add to the potential energy of the electron arising from the coulomb attraction to the nucleus the energy arising from the external field. A simplified quantum-mechanical calculation (Pitzer, 1953, p. 69) leads to the approximate value for hydrogen $\alpha = 4a_0^3$, where a_0, the "radius" of the hydrogen atom, is $0.528\ 10^{-8}$ cm. A correct calculation (Pauling and Wilson, 1935, pp. 227–229) yields $\alpha = 9/2a_0^3$. More generally, the electronic polarizability will be a function of $\overline{r^3}$, the mean cube radius of the electronic density distribution, just as the diamagnetic susceptibility measures the mean square radius. It is historically interesting that the first determination of the radius of the O^{--} ion was made precisely from a consideration of polarizability.

Pauling (1927) suggested that the polarizability of an atom should be given by the relation

$$\alpha = 0.281 \sum_{0}^{In} \frac{(5n^6 + 7n^4)(2l+1)}{(Z - \sigma_{nl})^4}$$

where n and l are the two first quantum numbers of an electron, σ_{nl} is an appropriate screening factor, the summation being carried over all electrons in the atom. Slater (1951, p. 204) points out that as the radius of an orbit with quantum number n is roughly proportional to $n^2/(Z-s)$, where Z and s are, as usual, the charge on the nucleus and the Slater screening factor, the polarizability should be proportional to

$$\left(\frac{n^2 a_0}{Z-s}\right)^3;$$

the proportionality factor would be 4.5 for $n=1$, 1.1 for $n=2$, 0.63 for $n=3$, etc. The Slater rule is somewhat easier to apply than the Pauling formula.

The value for hydrogen ($9/2\ a_0^3$) cannot be checked because of the absence of measurements on *atomic* hydrogen. For the helium atom, the experimental value of α is 0.205×10^{-24} cm.^{3}. Pauling and Wilson (1935, pp. 226–229) calculate values ranging from 0.15 to 0.23 Å^3, depending on the choice of wave function. The Slater rule gives $\alpha = 0.27$ Å^3. Further comparisons are listed in Table VIII.

We note the very small polarizability of the smaller cations, as compared with that of large anions.

Polarizability of ions in solution and certain crystals obey an additivity law similar to that followed by ionic diamagnetic susceptibilities. Tables of empirical polarizabilities have been set up in this way (see Kittel, 1953, p. 97).

In Table IX are listed the values of the polarizability of several compounds, computed by adding the Slater values of the polarizability

TABLE VIII. COMPARISON OF THE POLARIZABILITY OF VARIOUS IONS CALCULATED BY PAULING (1927) AND BY THE SLATER RULE

	Polarizability of ions, in Å^3,	
	According to Pauling (1927)	Calculated by Slater rule
O^{--}	3.88	1.46
Be^{++}	0.008	0.026
Mg^{++}	0.094	0.17
Al^{3+}	0.052	0.12
Si^{4+}	0.0165	0.08

of the component ions. These values may be compared with the experimental values

$$\alpha = \frac{3V}{4\pi N}\frac{n^2-1}{n^2+2},$$

n being the index of refraction for the sodium D line, or an arithmetic mean of the indices for non-cubic crystals.

The agreement between figures in the two columns is surprisingly good, when it is remembered that the Lorentz-Lorenz formula (11) is strictly applicable only to substances with high symmetry, and that the Slater rule is only approximate as it neglects the difference between orbitals of same principal quantum number but different l. Where disagreement exists is it not an indication of strong covalent bonding, as the following values (Table X) for covalent vs. ionic structures show.

TABLE IX. COMPARISON OF POLARIZABILITIES OF VARIOUS COMPOUNDS, DERIVED FROM INDICES OF REFRACTION OR CALCULATED BY ADDITION OF POLARIZABILITIES OF IONS

	Polarizability of compounds (in units of 10^{-24} cm.^{3})	
	$\alpha = \frac{3V}{4\pi N}\frac{n^2-1}{n^2+1}$	$\alpha = \Sigma\, n_1\alpha_1$ (Calculated by Slater rule)
BeO	1.31	1.49
MgO	1.75	1.63
Al_2O_3	4.18	4.62
$MgAl_2O_4$	6.2	6.25
SiO_2 (quartz)	2.86	3.00
SiO_2 (cristobalite)	2.90	3.00
$BeAl_2O_4$	5.65	6.11
Mg_2SiO_4	6.45	6.26
$MgSiO_3$	4.72	4.63

TABLE X. CALCULATED AND EXPERIMENTAL POLARIZABILITY OF MgO AND BeO

	Polarizability (10^{-24} cm.^{3})	
	Calculated	Experimental
Mg+O	6.83	1.75
Mg^++O^-	3.30	
Mg^{++}+O^{--}	1.63	
Be+O	3.50	1.31
Be^++O^-	1.86	
Be^{++}+O^{--}	1.49	

Strictly speaking, the polarizability of a covalent compound need not be equal to the sum of the polarizabilities of its constituents; the correction for covalency is, however, small, as shown by diamond: the polarizability of the isolated carbon atom, computed by the Slater rule, is 1.2×10^{-24} cm.^{3}; the experimental value for diamond is 0.84×10^{-24}.

As the polarizabilities of the cations are small and not likely to be much in error, we have computed the value of the polarizability of the oxygen that would give perfect agreement with experimental data. Results are as follows:

TABLE XI. POLARIZABILITY OF THE OXYGEN ION IN VARIOUS COMPOUNDS

MgO	1.58×10^{-24}
Mg_2SiO_4	1.51
$BeAl_2O_4$	1.50
$MgSiO_3$	1.49
$MgAl_2O_4$	1.45
SiO_2 (quartz)	1.39
SiO_2 (cristobalite)	1.41
Al_2O_3	1.31
BeO	1.28
$CaCO_3$	1.31
Al_2SiO_5 (sillimanite)	1.40
Al_2SiO_5 (andalusite)	1.39
Al_2SiO_5 (kyanite)	1.34
$Mg_3Al_2Si_3O_{12}$ (pyrope)	1.39
Average	1.41

The average of these 14 values, 1.41, is very close to the value for O^{--} obtained by the Slater rule (1.46). It is interesting that the cube root of the polarizability, which might be taken as an empirical radius,

is 1.16 A for O in MgO; this is precisely the distance at which the electron density around the O sites tails off. Similarly for $CaCO_3$: the empirical radius of $\sqrt[3]{1.31}=1.1$ is that which one would compute from the C-O distance (1.27 Å) assuming that the 3 oxygens surrounding carbon are just touching.

The electronic polarizability of an ion, as we have seen, is a function of the average radius of the electronic density; it should therefore be closely related to the ionic radius itself. We thus expect a relationship between the index of refraction of a compound and the radii of its constituent ions. Kordes (1956) has found empirically a relationship of this type. The "optical" ionic radii computed by him from refractive indices agree well with the conventional ionic radii, corrected where necessary for coordination number. He finds no indication of covalent bonding either in SiO_2 or in grossularite ($Ca_3Al_2Si_3O_{12}$).

In summary, the polarizability of compounds computed by adding the polarizabilities of their ions agrees with experimental values, if one uses the Slater rules to determine the polarizability of the ions. Polarizability gives no clear evidence of covalent bonding in any of the compounds considered.

Ionic Polarization

Consider a substance consisting of positive and negative ions. Under the influence of an external electrical field, the positive and negative ions will be displaced in opposite directions; these displacements produce a polarization which contributes to the dielectric constant an amount which is proportional to the net charges on the ions and to their displacement. These displacements, in turn, depend on the restoring forces between ions; if one assumes, for instance, a restoring force $f=Kx$ proportional to the displacement x, x will be given by the simple relation $Ee=Kx$ where e is the charge on the ion, E the field acting on it, and K is the force constant. The induced dipole is ex, and the polarizability $\alpha=ex/E=e^2/K$.

Now if the restoring force between two particles of mass m_1, m_2 is proportional to the displacement, the particles will oscillate with a frequency

$$\omega_0 = \sqrt{K/\mu}$$

where μ is the reduced mass

$$\frac{1}{\mu}=\frac{1}{m_1}+\frac{1}{m_2}.$$

This frequency usually falls in the infrared. In the visible part of the spectrum the frequency of the electric field is much greater than the natural frequency of oscillation of the ions which remain essentially un-

disturbed; the ionic polarization does not contribute to the dielectric constant or to the index of refraction, which arises entirely from the electronic polarizability discussed above. For a static electric field, or in general for fields with frequency less than ω_0, the oscillations of the ions contribute a polarization which increases the dielectric constant. The dielectric constant for static fields is thus found to be greater than n^2 by an amount $\Delta\epsilon$, n^2 being the square of the refractive index extrapolated to infinite wave length by a suitable dispersion formula. $\Delta\epsilon$ thus measures the charge on the ions and the force constant. As the force constant also determines the compressibility, one expects a relation between the actual charge on the ions, the compressibility, $\Delta\epsilon$, and the fundamental frequency ω_0. Thus if $\Delta\epsilon$ and ω_0 or the compressibility are known, it should be possible to determine the actual charge on the ions. Conversely, one could also compute the compressibility for purely ionic structures and compare the calculated and experimental values.

There is an abundant literature on the subject (Højendahl, 1938; Szigeti, 1949, 1950; Mott and Gurney, 1948, pp. 20–21; Kittel, 1953, pp. 98–100; Born and Huang, 1954, chap. II). Difficulties arise from a correct evaluation of E_{loc}, the field acting on a particle inside the structure. It was pointed out earlier that both the Drude formula ($E_{\text{loc}}=E$) and the Lorentz-Lorenz formula ($E_{\text{loc}}=E+4/3\ \pi P$) are approximate. The field is not necessarily homogeneous and need not be the same at various points within an ion of finite size. The ionic polarization also affects the electronic polarization, and the ions may overlap and thus become deformed. As mentioned before, Mott and Gurney use the more general relation (10) $E_{\text{loc}}=E+\gamma 4/3\ \pi P$ where γ is an empirical factor to be determined from the dielectric constant and compressibility; they find rather good agreement for alkali halides if $\gamma=0$; but they believe that difficulties in estimating γ preclude accurate calculation of the dielectric constant or of the exact charge distribution; they point out that homopolar bonding will increase the dielectric constant, and recall that the high dielectric constant of rutile (about 100) and other salts has been ascribed to an effect of this type; of which more later.

Szigeti (1949) recognized that the polarizability should depend on the wave length and character of the wave (whether longitudinal or transverse); the Lorentz-Lorenz formula (11) should hold for the polarizablity of a sphere in long waves, whereas the Drude formula (7) should be applicable to short transverse waves. Taking into account possible overlap of ions, and the interdependence of electronic and ionic polarizabilities, Szigeti derived a relation between $\Delta\epsilon$, n, the frequency of the transverse optical branch and the effective charge sze on the ion, where z is the valency and e the charge of one electron. Values of s for alkali

halides range from 0.69 (for KI) to 0.93 (for NaF); s is usually somewhat larger than the ionic character obtained from Pauling's curve, but does not vary systematically with the Pauling electronegativity scale: for instance, KI and RbI should have the same amount of ionic character according to Pauling, whereas s is 0.69 for KI but 0.89 for RbI. One is surprised to find $s=1$ for CuBr, and $s=1.10$ for CuCl. Szigeti obtains $s=0.88$ for MgO, taking the wave length of the fundamental infrared absorption band to be 17.3 μ; if one uses Saksena's (1956) value 25.2 μ, s comes out at 0.62, although the agreement between calculated and measured compressibility is much improved.

It seems difficult to ascertain whether Szigeti's results bear significantly on the matter of ionic vs. covalent bonding. Szigeti believes that the deviation of s from the value unity is caused mainly by the mutual distortion of neighboring ions owing to their overlap; this is independent of, and need not reflect on, the total number of electrons on the ion.

The view was expressed above that homopolar binding might tend to increase the dielectric constant, and that the high dielectric constant of compounds such as rutile has to be ascribed to this effect. Other explanations are also possible. Szigeti finds $s=0.7$ for rutile, which implies a notably ionic structure. The Clausius-Mosotti equation, which is based on the Lorentz field $E_{\text{loc}}=E+4/3\,\pi P$, may be rewritten

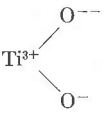
$$\epsilon=\frac{1+\frac{8\pi}{3}\frac{N}{V}\alpha}{1-\frac{4\pi}{3}\frac{N}{V}\alpha}$$

which shows that ϵ may be very large if

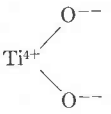
$$\frac{4\pi}{3}\frac{N}{V}\alpha$$

happens to be sufficiently close to 1. For static or low frequency fields, α must of course include the ionic and electronic polarizabilities.

The electronic polarizability of rutile is interesting: from the average value of the index of refraction (2.705), one finds $\alpha=5.1\times10^{-24}$ cm^3. The polarizability of Ti^{4+} is small (0.19 according to Pauling; 0.45 according to the Slater formula), so that the polarizability of O^{--} should be 2.3×10^{-24} or more, which is much greater than in the other oxides considered so far. It is actually not necessary to resort to covalent bonding to account for the anomaly if one notices that the ionization potentials of $3d$ and $4s$ electrons in titanium are almost equal; thus the Ti^{+3} ion would have a large polarizability due to its remaining ($4s$) electron, and a small admixture of the ionic state



to the state



would appreciably increase the electronic polarizability.

In conclusion, it would appear once again that there is nothing in the theory of electronic or ionic polarizability that compels us to abandon a simple ionic representation of the compounds presently under consideration.

Coordination Numbers

In covalent bonds the coordination number of an atom depends essentially on the ease with which it can form hybrid orbitals of various types. On the other hand, the coordination number of a cation is predictable, in the purely ionic model, by the simple radius-ratio rule: the number of nearest neighbors depends solely on the ratio of the ionic radii of the anion and cation. According to this rule, one generally expects to find small cations in a lower coordination than large ones. At first sight, the structure of spinel ($MgAl_2O_4$) in which Mg is in 4-coordination and Al in 6-coordination, appears anomalous. There has been a tendency to explain such anomalies in radius-ratio rules by recourse to covalent bonding. As it turns out, the structure of any particular member of the spinel group can be simply explained in terms of an ordinary coulomb attraction between charged ions, the Madelung constant being larger for the normal than for the inverse structure for large values of the oxygen parameter u (Gorter, 1954). One could argue, however, that the tendency of any particular ion to occupy 4-coordinated (A) sites rather than 6-coordinated (B) sites, or vice versa, determines in the first place whether the structure will be normal or inverse, the oxygen parameter u then adjusting itself so as to minimize the coulomb energy. It is thus interesting to compute the energy that would be necessary to transfer any particular ion from, say, a 6-coordinated (B) site to a 4-coordinated (A) site of the spinel structure. X-ray, crystallographic, and magnetic data are fortunately available from which the distribution of the various ions among the A and B sites may be calculated in minerals and artificial "ferrites" with the spinel structure. Consider the general case of a spinel with formula $MN_{2-t}Q_tO_4$ in which M is a divalent element (Mg, Ni, Fe^{2+}, etc.),

while N and Q are trivalent elements (Al, Fe^{3+}, etc.). Assume the distribution to be

$$M_xN_yQ_z[M_{1-x}N_{2-t-y}Q_{t-z}]O_4$$

where brackets indicate 6-coordinated cations in B sites, and $x+y+z=1$. The configurational entropy is $S=K\ ln\ W$ where K is Boltzmann's constant and

$$W = \frac{1!(2-t)!t!}{x!y!z!(1-x)!(2-t-y)!(t-2)!}.$$

If U is the internal energy and F the Helmholtz free energy $F=U-TS$, a simple algebraic calculation yields

$$\begin{aligned}\frac{\partial F}{\partial x} &= U_x' - KT\ ln\frac{1-x}{x}\\ \frac{\partial F}{\partial y} &= U_y' - KT\ ln\frac{2-t-y}{y}\\ \frac{\partial F}{\partial z} &= U_z' - KT\ ln\frac{t-z}{z}\end{aligned} \tag{12}$$

when $U_x'=\delta U/\delta x$, etc. Since $x+y+z=1$, F is minimum when

$$\frac{\partial F}{\partial x} = \frac{\partial F}{\partial y} = \frac{\partial F}{\partial z}$$

so that in the equilibrium configuration we have (Smart, 1954)

$$\begin{aligned}U_x' - U_y' &= KT\ ln\frac{(1-x)y}{x(2-t-y)}\\ U_y' - U_z' &= KT\ ln\frac{(2-t-y)z}{(t-z)y}\\ U_z' - U_x' &= KT\ ln\frac{(t-z)x}{(1-x)z}.\end{aligned} \tag{13}$$

In these relations, $U_x'-U_y'$ is the energy necessary to move an atom of M from a B to an A site, an atom of N being simultaneously transferred from an A to a B site. These energy differences may thus be calculated from measured values of x, y and z. Note that only differences such as $U_x'-U_y'$ can be gotten in this way; the values of U_x', U_y', U_z' can be obtained separately only on the assumption that enough vacancies exist in A and B sites that the relation $x+y+z=1$ need not hold; that is, that one could transfer an atom from a B to an A site without simultaneously moving another atom from A to B.

A carefully studied compound of this type is $MgFe^{3+}O_4$, with structure $Mg_xFe_y^{3+}[Mg_{1-x}Fe_{2-y}^{3+}]O_4$, for which x has been determined as a function of temperature by Pauthenet and Bochirol (1951) (see also Bertaut, 1951). For a binary compound, equations (13) simply reduce to

$$U_x' - U_y' = KT\ ln\frac{(1-x)^2}{x(x+1)}. \tag{14}$$

The calculated values vary slightly with temperature, due perhaps to incomplete annealing at lower temperature; at high temperature (1200° C.) the authors find $U_x' - U_y' = 0.11$ e.v. A calculation based on the assumption stated above gives

$$U_x' = +0.15 \text{ e.v.} = 3500 \text{ cal/mole}$$
$$U_y' = +0.04 \text{ e.v.}$$

only the difference between these two quantities being truly significant.

Similar calculations have been carried out for other compounds and are listed in Table XII. Data are from Gorter (1954); Greenwald, Pickart and Grannis (1954); Bacon and Roberts (1953). In all the instances listed, it has been assumed that measured values of x, y, and z are those for specimens perfectly quenched from a high temperature (1200° C.). This may not be generally true, as some workers used annealed specimens; some of the energies listed in Table XII may thus be too large by a factor of 2 or 3.

TABLE XII. ENERGIES (IN ELECTRON VOLTS) TO TRANSFER ATOMS FROM 6- TO 4-COORDINATES SITES IN SPINELS

Compound and distribution	U'_{Mg}	U'_{Ni}	$U'_{Fe^{3+}}$	U'_{Al}	Transfer energies
$Mg_{0.22}Fe_{0.78}{}^{3+}[Mg_{0.78}Fe^{3+}{}_{1.22}]O_4$	+0.15		+0.04		$U'_{Mg} - U'_{Fe} = 0.11$
$Mg_{0.53}Fe^{3+}{}_{0.47}[Mg_{0.47}AlFe^{3+}{}_{0.53}]O_4$	−0.015		+0.015		$U'_{Mg} - U'_{Fe} = -0.03$
$Fe^{3+}{}_{0.96}Al_{0.04}[Fe^{2+}Al_{0.16}Fe^{3+}{}_{0.84}]O_4$			−0.015	+0.18	$U'_{Fe^{3+}} - U'_{Al} = -0.19$
$Ni_{0.15}Fe^{3+}{}_{0.24}Al_{0.61}[Ni_{0.85}Fe^{3+}{}_{0.91}Al_{1.14}]O_4$		+0.221	−0.41	+0.1	$U'_{Fe^{3+}} - U'_{Al} = -0.51$
$Ni_{0.05}Fe^{3+}{}_{0.68}Al_{0.27}[Ni_{0.95}Fe^{3+}{}_{0.32}Al_{0.73}]O_4$		+0.375	−0.1	+0.12	$U'_{Fe^{3+}} - U'_{Al} = -0.22$

The energies listed in Table XII, as explained, are approximate; yet their magnitude is very striking in being so small. Compare, for instance, the promotion energies of aluminum to a valence state sp^3 (tetragonal hybrid; 3.6 e.v.) or to a d state (octahedral hybrid; 7.5 e.v.). Clearly, the equilibrium distribution of ions among the 4- and 6-coordinated positions in the spinel structure depends on very small energy differences that do not suggest any fundamental difference in type of binding. The transfer energy for a given pair (e.g., Al-Fe^{3+}) also varies appreciably as a function of composition, or of cell dimensions. The general trend for Mg is to go into A sites only when the structure is such that the radii of the A and B sites are nearly equal; when the radius of a B site becomes appreciably (20%) larger than that of an A site, the transfer energy of Mg becomes positive, as in $MgFe_2O_4$. Aluminum has precisely the opposite tendency, its transfer energy becoming more and more positive as the ratio r_6/r_4 becomes smaller. In $MgAl_2O_4$, $r_6 = r_4$; accordingly Al is in B sites and Mg in A sites. Such relationships are not easily explainable in terms of purely covalent binding.

It would seem to follow from these considerations that a departure from the usual coordination number (e.g., Mg in 4- rather than 6-coordi-

nation) does not necessarily imply an appreciable change in the amount of covalent bonding; simple electrostatic considerations may still be used to predict coordination numbers in the spinel structure.

It is interesting to note that Loeb and Goodenough (1955), who rely on covalent bonding to explain a number of structural features of spinels, consider that Mg and Al in spinels are essentially electrovalent, in agreement with our conclusion. Covalent effects occur only with transition or heavier elements.

It is unfortunate that so few data should be available on the physical and thermochemical properties of the aluminum silicates Al_2SiO_5, in which the aluminum coordination is either 6 (kyanite), or 6 and 5 (andalusite), or 6 and 4 (sillimanite). As far as is known, it would seem that the free energies of these three compounds do not differ by more than a few thousand, or even perhaps a few hundred, calories at room temperature and ordinary pressure. The entropy of any of these 3 phases is almost exactly the sum of the entropies of the oxides, corrected for density differences. The polarizability of the oxygen ion (Table XI) is the same in sillimanite and andalusite; in kyanite it is exactly equal to the average for quartz and corundum. Here again, it seems unlikely that the change in coordination should reflect any notable change in electronic density distribution and bond type.

This does not mean that coordination numbers cannot, in some rare instances, be taken to indicate the presence of a notable amount of covalent bonding. ZnO is a good example. Surely, as has been pointed out many times, the difference between MgO (6-coordination, NaCl structure) and ZnO (4-coordination, wurtzite structure) cannot be explained on the basis of radius-ratio considerations, as Mg^{++} and Zn^{++} are said to have rather similar radii. However, tetrahedral coordination presumably requires hybridization, the ease of which may be roughly evaluated by comparing the ionization potentials of successive electron shells or subshells. For instance, the difference in ionization potential of $2p$ and $2s$ electrons in C is 0.7 atomic units (1 atomic unit = 13.54 e.v.); $3p-3s$ in silicon is 0.5; $4s-3d$ in Zn is 0.5; etc. By contrast, consider $3s-2p$ in Mg = 3.1, $4s-3p$ in Ca = 1.45. Thus one expects hybridization, and formation of tetrahedral coordination, to occur readily in C, Si, Zn, but not in Mg, Ca, etc. It is interesting that ZnO and BeO are actually the only oxides of bivalent elements that occur in either the zincblende or wurtzite structures; and the 4-coordination of Be in BeO is readily explained on radius-ratio considerations alone (radius of $Be^{++} = 0.35$). In the same way, one expects on general grounds that carbon would occur covalently either in 2-(CO_2) or 4-coordination (CH_4). The occurrence of the CO_3 group in carbonates is difficult to explain (Fyfe, 1954); yet it follows directly from radius-ratio rules.

Summary and Conclusions

We have examined such physical properties of simple oxides and silicates of Mg and Al as could lead, independently of any chemical considerations, to an evaluation of the ionic or covalent character of these compounds. We noticed first that *lattice energies* computed for purely ionic structures usually agree well with "experimental" values, as they also do for some sulfides and selenides with less pronounced ionic characteristics. The *Cauchy relations* between elastic coefficients offer no critical test of ionicity; they point to the existence of non-central forces which may arise from a mutual deformation of ions rather than from directed bonds of covalent type. *X-ray data* on MgO are interesting: they show the presence of nearly perfectly spherical units, with a charge distribution suggesting a structure intermediate between Mg^{++}—O^{--} and Mg^{++}—O^{-}, the remaining electrons are spread out evenly without any indication of localized bonds. The interpretation of the *diamagnetic susceptibility* offers some difficulty. Experimental determinations are few and likely to be inaccurate because of the presence of uncontrolled amounts of paramagnetic impurities. Results for SiO_2 are quite consistent with a fully ionic structure Si^{++}—O^{--}, and the same applies, to a lesser degree, to Al_2O_3. For MgO the susceptibility suggests a structure more ionic than Mg^{++}—O^{--}, and one suspects an appreciable Van Vleck term related to the interstitial electrons mentioned above. The *electronic polarizability* is again consistent with a fully ionic structure, the average polarizability of oxygen in a number of compounds being almost exactly that predicted by the Slater rule for O^{--}. The *ionic* polarizability shows departures from the values expected for purely ionic structures, although differences may be due in large part to theoretical difficulties in evaluating the internal field; the degree of covalency derived from the ionic polarizability does not agree with that calculated from the electronegativity values. *Coordination numbers* are probably rather poor indicators of covalent vs. ionic character. The calculated values of the *transfer energy* required to interchange 6-coordinated and 4-coordinated cations in spinels turn out to be so small as to suggest very little difference in bond character in the two sites.

Thus it would seem that on the whole, the physical properties of the compounds studied are much more easily explained on ionic than on a covalent basis. This is, surprisingly, particularly true of SiO_2, which is generally regarded as at least 50% covalent. The agreement between experimental data and values calculated for purely ionic structures is by no means perfect; but the fault may reside in the theory. There is, of course, ample evidence that ions do not behave as rigid spheres; they are deformable, as the index of refraction readily shows. This polarizability, however, seems calculable on a purely electrostatic theory and is there-

fore more amenable to treatment than when interpreted in terms of covalent binding. The polarizability will lead to difficulties in estimating elastic coefficients, but would not seem to be of major importance in other calculations.

We conclude, therefore, that for practical purposes it is legitimate to consider the compounds under consideration as purely ionic.

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