tions of the total pressures from ideality, at 20 mole % of the lighter constituent, are as follows: butane-pentane, +4; butane-heptane, 0; pentane-heptane, +7; butane-benzene, +64; butane-straw oil, —2.6. These deviations are discussed in the light of polarity and the internal pressure of the molecules. A critical study is offered of related data from the literature.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

THE SIZES OF IONS AND THE STRUCTURE OF IONIC CRYSTALS

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The Wave-Mechanics Picture of the Atom

In recent years the old quantum theory, associated principally with the names of Bohr and Sommerfeld, encountered a large number of difficulties, all of which vanished before the new quantum mechanics of Heisenberg.[2] Because of its abstruse and difficultly interpretable mathematical foundation, Heisenberg's quantum mechanics cannot be easily applied to the relatively complicated problems of the structures and properties of many-electron atoms and of molecules; in particular is this true for chemical problems, which usually do not permit simple dynamical formulation in terms of nuclei and electrons, but instead require to be treated with the aid of atomic and molecular models. Accordingly, it is especially gratifying that Schrödinger's interpretation of his wave mechanics[3] provides a simple and satisfactory atomic model, more closely related to the chemist's atom than to that of the old quantum theory.

In Schrödinger's wave mechanics (which has been shown[4] to be mathematically identical with Heisenberg's quantum mechanics), a conservative Newtonian dynamical system is represented by a wave function or amplitude function ψ, which satisfies the partial differential equation

$$\Delta^2\psi + (8\pi^2/h^2)(W - V)\psi = 0 \qquad (1)$$

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[1] Fellow of the John Simon Guggenheim Memorial Foundation.

[2] Heisenberg, *Z. Physik*, **33**, 879 (1925). Born and Jordan, *ibid.*, **34**, 858 (1925). Born, Heisenberg and Jordan, *ibid.*, **35**, 557 (1926); etc. Heisenberg based his theory on the thesis that it should not contain reference to quantities which are in principle unobservable. It is of interest that G. N. Lewis, in 1923, suggested this idea, writing.... "we should look for no effects which depend upon the momentary position of any electron in its orbit" ("Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, **1923**, p. 52).

[3] Schrödinger, *Ann. Physik*, **79**, 361, 489; **80**, 437; **81**, 109 (1926); *Phys. Rev.*, **28**, 1049 (1926).

[4] Schrödinger, *Ann. Physik*, **79**, 734 (1926). Eckart, *Phys. Rev.*, **28**, 711 (1926).

In this equation W and V are the energy constant and the potential energy, respectively; the indicated partial differential operations involve coordinates whose line element is

$$ds^2 = 2T dt^2 \tag{2}$$

in which T is the kinetic energy expressed as a function of the velocities; ψ must be continuous, single-valued, and bounded throughout the entire region traversed by the coördinates. Only certain functions (called eigenfunctions) satisfy these requirements in any given problem. In the case of the hydrogen atom these functions, Ψ_{nlm}, are known;[3,4,5] the one corresponding to the lowest quantum state is

$$\Psi_{100} = -\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \cdot \epsilon^{-\frac{\xi}{2}} \tag{3}$$

with

$$\xi = 2\frac{Z}{a_0}r \tag{4}$$

and

$$a_0 = \frac{h^2}{4\pi^2 me^2} = 0.532 \text{ Å}.$$

Schrödinger has interpreted the quantity $\psi\tilde{\psi}$ ($\tilde{\psi}$ being the conjugate complex of ψ) as giving the probability of the occurrence of the corresponding microscopic state of the system. For the hydrogen atom $\Psi\tilde{\Psi}$ accordingly gives the *electron density* about the nucleus. This may be considered as an actual stationary distribution of the individual electron throughout space, following Schrödinger, or as a time average of all the positions assumed by a point electron. The electron density ρ for the lowest quantum state of a hydrogen-like atom is, then,

$$\rho = \Psi_{100}^2 = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \epsilon^{-\xi} \tag{5}$$

In Fig. 1 there are represented the eigenfunction Ψ_{100}, the electron density ρ, and the electron distribution function $D = 4\pi r^2\rho$ for the hydrogen atom as functions of r.

This model of the hydrogen atom accordingly consists of a nucleus embedded in a ball of negative electricity—the electron distributed through space. The atom is spherically symmetrical. The electron density is greatest at the nucleus, and decreases exponentially as r, the distance from the nucleus, increases. It remains finite, however, for all finite values of r, so that the atom extends to infinity; the greater part of the atom, however, is near the nucleus—within 1 or 2 Å.

A similar model for many-electron atoms has been developed,[6] by considering each electron to be hydrogen-like, but under the influence of an effective nuclear charge $(Z - S_S)e$, in which S_S is called the size-screening constant. It is found that atoms and ions containing only S electrons (with the quantum number l equal to zero) and completed sub-groups of

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[5] Waller, *Z. Physik*, **38**, 635 (1926).

[6] Pauling, paper submitted to *Proc. Roy. Soc.*

electrons are spherically symmetrical. In Fig. 2 is shown the electron distribution D as a function of r for the sodium ion and the chloride ion. The chloride ion may be described in the following words: the nucleus is embedded in a small ball of electricity, consisting of the two K electrons, with a trace of the L and M electrons; surrounding this are two concentric shells, containing essentially the eight L and the eight M electrons. In general, an atom or ion consists of the nucleus in the K electron ball, and surrounded by more or less sharply demarcated shells, one for each succeeding value of the principal quantum number n.

Since every atom extends to an unlimited distance, it is evident that no single characteristic size can be assigned to it. Instead, the apparent atomic radius will depend upon the physical property concerned, and will differ for different properties. In this paper we shall derive a set of ionic radii for use in crystals composed of ions which exert only a small deforming force on each other. The application of these radii in the interpretation of the observed crystal structures will be shown, and an attempt made to account for the formation and stability of the various structures.

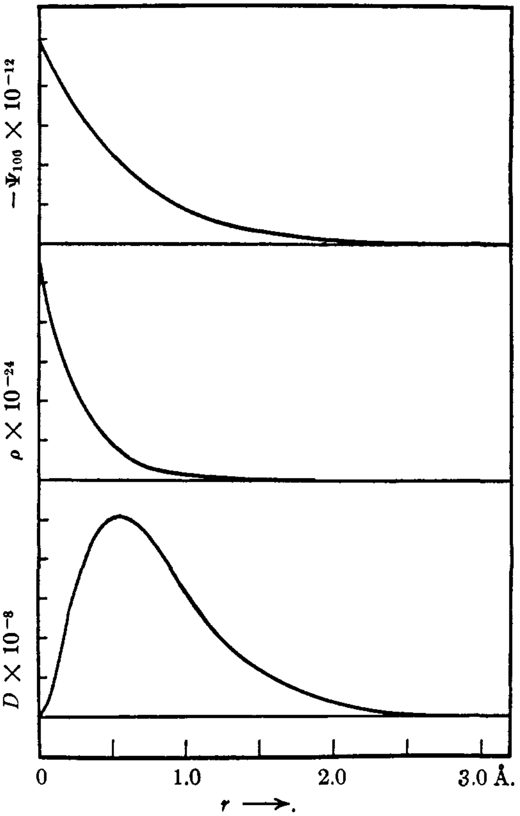

Fig. 1.—The eigenfunction Ψ_{100}, the electron density $\rho = \Psi_{100}^2$, and the electron distribution function $D = 4\pi r^2\rho$ for the lowest state of the hydrogen atom, as functions of r.

The Forces in Crystals

Hitherto it has been generally assumed that the repulsive forces between atoms arise from the interaction of the quadrupole (and higher) moments of the atoms, that is, from their departure from spherical symmetry.[7]

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[7] For example, (a) Born and Landé, *Sitzber. preuss. Akad. Wiss.*, **1918**, 1048. (b) Born, *Verh. d. Deutsch. phys. Ges.*, **20**, 230 (1918). (c) Landé, *Z. Physik*, **1**, 191 (1920); (d) **2**, 83, 87, 80 (1920). (e) Smekal, *ibid.*, **1**, 309 (1920). (f) Rella, *ibid.*, **3**,

This assumption is no longer valid; in its place the wave mechanics provides the simple explanation that the repulsive forces arise from the interpenetration of the atoms. As a simple example, we may consider the hydrogen ion and the chloride ion; according to the wave mechanics the potential energy of these two ions at a distance R apart, assuming that no deformation occurs, is[6]

$$\Phi_{\mathrm{HCl}} = -\frac{e^2}{R} + \frac{e^2}{18R} e^{-\xi} (\xi^5 + 2\xi^4 + 12\xi^3 + 48\xi^2 + 120\xi + 144) \qquad (6)$$

in which $\xi = (2/3)[(Z - S_S)/a_0]R$. The first term is the Coulomb potential energy of the two ions, and the second term arises from the penetration of the hydrogen ion in the chloride ion, and the resultant repulsion of the two similarly charged nuclei.[8]

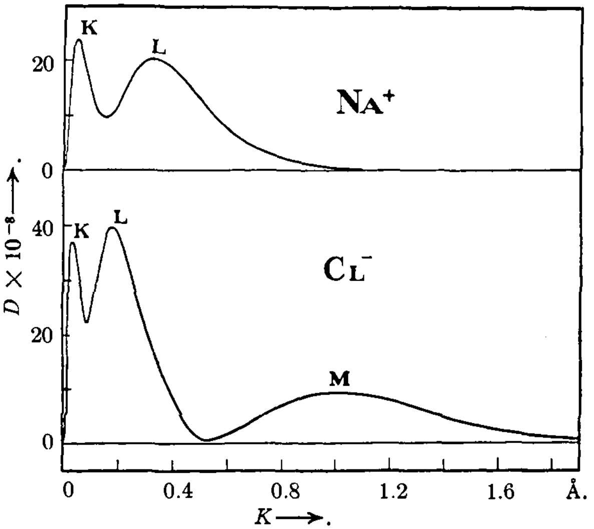

Fig. 2.—The electron distribution $D = 4\pi r^2\rho$ as a function of r for the sodium ion and the chloride ion.

157 (1920). The idea that the repulsive forces arise from the interaction of "cubical" ions (with electrons at cube corners) has been made the basis of a very extensive discussion [by Fajans and Herzfeld, *ibid.*, **2**, 309 (1920). Grimm, *Z. physik. Chem.*, **98**, 353 (1921); **101**, 403 (1922); **102**, 113, 141, 504 (1922); **119**, 254 (1926); **122**, 177 (1926); etc.] in which the sizes of these hypothetical cubes are estimated from experimental data for a large number of ions, and the attempt is made to bring these sizes into agreement with the Bohr atomic model, and to explain with them the physical properties of substances. Since, accepting the wave mechanics, we now believe that most ions are spherically symmetrical, and that the repulsive forces have an entirely different origin, no physical significance can be attributed to these cubical ion sizes. It is worthy of mention that the cubical ion sizes derived are in general about one-half of our univalent crystal radii; so that discussions involving their relative values are still valid.

[8] The expression for the potential energy of a potassium ion and a chloride ion, for example, is similar to that of Equation 6, but is still more complicated.

The potential energy of an ionic crystal (ions of valence z) may be written $\Phi = -\alpha(e^2z^2)/R + \varphi(R)$, the first term representing the Coulomb energy, and the second the potential of the repulsive forces. Equation 6 suggests a simple form for $\varphi(R)$, namely

$$\varphi(R) = \beta_m R^m e^{-\gamma R} \tag{7}$$

It has been customary, however, to use the expression

$$\varphi(R) = \beta_n R^{-n} \tag{8}$$

widely applied by Born and his co-workers. The constants β_m and γ (for a given choice of m) or β_n and n may be determined from the experimental measurements of the size of the unit of structure in crystals and of their compressibility, which provide values of $\mathrm{d}\varphi/\mathrm{d}R$ and $\mathrm{d}^2\varphi/\mathrm{d}R^2$ for $R = R_0$, the equilibrium distance. For many calculations only these two derivatives are significant, so that it is immaterial which form of $\varphi(R)$ is used; examples of such calculations will be given later. For others the value of $\varphi(R_0)$ itself is needed, which depends on the particular empirical equation used. For example, the values obtained for the crystal energy Φ by the use of Equation 8 and by the use of Equation 7 (with $m = 0$) differ by about 1%, or around 2000 cal. per mole for crystals such as sodium chloride.

The Sizes of Ions in Crystals

As a first approximation, each electron in a many-electron atom can be considered to have the distribution in space of a hydrogen-like electron under the action of the effective nuclear charge $(Z-S_S)e$, in which S_S represents the screening effect of inner electrons. In the course of a previous investigation,[6] values of S_S for a large number of ions were derived.

TABLE I

THE SIZE-SCREENING CONSTANT

Structure	Z_0	Sub-group	S_{S0}	ΔS_S
He	2	K	0.188	0
Ne	10	L_{11}	2.84	0
		L_{21} L_{22}	4.52	
Ar	18	M_{11}	9.15	0.07
		M_{21} M_{22}	10.87	
Kr	36	N_{11}	23.91	.25
		N_{21} N_2	26.83	
Xe	54	O_{11}	38.68	.49
		O_{21} O_{22}	41.80	
[Cu$^+$]	28	M_{11}	10.9	.03
		M_{21} M_{22}	13.15	
		M_{32} M_{33}	17.7	
[Ag$^+$]	46	N_{11}	27.9	.31
		N_{21} N_{22}	30.3	
		N_{32} N_{33}	35.1	
[Au$^+$]	78	O_{11}	54.2	.67
		O_{21} O_{22}	57.0	
		O_{32} O_{33}	62.7	

For an ion of nuclear charge Ze, the size-screening constant for a given electron is

$$S_S = S_{S_0} + (Z - Z_0)\Delta S_S \tag{9}$$

Values of S_{S_0}, ΔS_S and Z_0 for the outer electrons for various ionic structures are given in Table I.

The size of an atom or ion is determined by the distribution of the outermost electrons, which are for neon the L_{21} L_{22}, for argon the M_{21} M_{22}, etc. Moreover, for similar ions the electron distribution is similar, but equivalent radii are in the inverse ratio of the corresponding effective nuclear charges. With this principle we shall obtain radii for ions, which we shall define in such a way as to fulfil the following condition: the sum of the radii of two ions equals the inter-ionic distance in a normal crystal composed of these ions with the sodium chloride structure.[9] As a starting point we shall use the following experimental inter-ionic distances, for crystals with the sodium chloride structure:[10] Na^+-F^-, 2.31; K^+-Cl^-, 3.14; Rb^+-Br^-, 3.43; Cs^+-I^-, 3.85 Å. The Cs^+-I^- distance is obtained by subtracting 2.7% from the experimental distance in the crystal with the cesium chloride structure; the justification for this will be given later. In addition we shall assume for Li^+ the radius 0.60 Å., obtained later from the experimental distance in lithium oxide. From these values all of our radii will be derived. By dividing these distances between the two ions concerned, with the use of the screening constants given in Table I, the radii for the alkali ions and the halogen ions given in Table II are obtained. For other ions with similar structures radii are also calculated by assuming them inversely proportional to the effective nuclear charge. These radii, given in parentheses in Table II are, however, not to be directly applied in the consideration of inter-ionic distances in crystals, for they are the radii which the ions would have *if they were univalent;* they provide, however, a measure of the relative sizes of ions of a given structure, that is, of their extension in space. The actual crystal has the following potential energy.

$$\Phi = -\alpha(z^2e^2)/R + \beta/R^n \tag{10}$$

For equilibrium, at $R = R_z$, we have the condition

$$(\mathrm{d}\Phi/\mathrm{d}R)_{R=R_z} = \alpha(z^2e^2)/R_z^2 - n\beta/R_z^{n+1} = 0 \tag{11}$$

or

$$R_z^{n-1} = n\beta/\alpha e^2 z^2$$

If the ions were univalent, but otherwise unchanged, the potential energy would be $\Phi_1 = -\alpha e^2/R + \beta/R^n$, and for equilibrium, with $R = R_1$

$$R_1^{n-1} = (n\beta)/(\alpha e^2) \tag{12}$$

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[9] A normal crystal is one in which contact (that is, strong repulsion) occurs only between adjacent anions and cations, and in which there is only so much deformation as that shown by the alkali halides.

[10] The crystal structure data are taken from Wyckoff, "International Critical Tables," except where otherwise noted. Inter-atomic distances referred to Goldschmidt are from Goldschmidt, *Skrifter Det. Norske Videnskaps-Akad. Oslo I. Matem.-Naturvid. Klasse*, **1926**, No. 2.

TABLE II

CRYSTAL RADII AND UNIVALENT CRYSTAL RADII OF IONS

			H^-	He	Li^+	Be^{++}	B^{+3}	C^{+4}	N^{+5}	O^{+6}	F^{+7}
			2.08		0.60	0.31	0.20	0.15	0.11	0.09	0.07
			(2.08)	(0.93)	(.60)	(.44)	(.35)	(.29)	(.25)	(.22)	(.19)
C^{-4}	N^{-3}	$O^=$	F^-	Ne	Na^+	Mg^{++}	Al^{+3}	Si^{+4}	P^{+5}	S^{+6}	Cl^{+7}
2.60	1.71	1.40	1.36		0.95	0.65	0.50	0.41	0.34	0.29	0.26
(4.14)	(2.47)	(1.76)	(1.36)	(1.12)	(.95)	(.82)	(.72)	(.65)	(.59)	(.53)	(.49)
Si^{-4}	P^{-3}	$S^=$	Cl^-	Ar	K^+	Ca^{++}	Sc^{+3}	Ti^{+4}	V^{+5}	Cr^{+6}	Mn^{+7}
2.71	2.12	1.84	1.81		1.33	0.99	0.81	0.68	0.59	0.52	0.46
(3.84)	(2.79)	(2.19)	(1.81)	(1.54)	(1.33)	(1.18)	(1.06)	(.96)	(.88)	(.81)	(.75)
					Cu^+	Zn^{++}	Ga^{+3}	Ge^{+4}	As^{+5}	Se^{+6}	Br^{+7}
					0.96	0.74	0.62	0.53	0.47	0.42	0.39
					(.96)	(.88)	(.81)	(.76)	(.71)	(.66)	(.62)
Ge^{-4}	As^{-3}	$Se^=$	Br^-	Kr	Rb^+	Sr^{++}	Y^{+3}	Zr^{+4}	Nb^{+5}	Mo^{+6}	
2.72	2.22	1.98	1.95		1.48	1.13	0.93	0.80	0.70	0.62	
(3.71)	(2.85)	(2.32)	(1.95)	(1.69)	(1.48)	(1.32)	(1.20)	(1.09)	(1.00)	(.93)	
					Ag^+	Cd^{++}	In^{+3}	Sn^{+4}	Sb^{+5}	Te^{+6}	I^{+7}
					1.26	0.97	0.81	0.71	0.62	0.56	0.50
					(1.26)	(1.14)	(1.04)	(.96)	(.89)	(.82)	(.77)
Sn^{-4}	Sb^{-3}	$Te^=$	I^-	Xe	Cs^+	Ba^{++}	La^{+3}	Ce^{+4}			
2.94	2.45	2.21	2.16		1.69	1.35	1.15	1.01			
(3.70)	(2.95)	(2.50)	(2.16)	(1.90)	(1.69)	(1.53)	(1.39)	(1.27)			
					Au^+	Hg^{++}	Tl^{+3}	Pb^{+4}	Bi^{+5}		
					1.37	1.10	0.95	0.84	0.74		
					(1.37)	(1.25)	(1.15)	(1.06)	(.98)		

From Equations 11 and 12 there is obtained

$$R_z = R_1 z^{-\frac{2}{n-1}} \tag{13}$$

From this equation we can calculate the actual crystal radius R_z (for use in normal sodium chloride type crystals) from R_1, the univalent crystal radius. A knowledge of the repulsion exponent n is needed, however. This can be derived from the experimental measurement of the compressibility of crystals. Born[11] and Herzfeld,[12] give the values in Table III, obtained in this way.

TABLE III

THE REPULSION EXPONENT FOR CRYSTALS

Crystal	n (Born)	n (Herzfeld)	n
NaCl	7.84	9.1	8
NaBr	8.61	9.5	8.5
NaI	8.45	..	9.5
KF	..	7.9	8
KCl	8.86	9.7	9
KBr	9.78	10.0	9.5
KI	9.31	10.5	10.5
RbBr	..	10.0	10
RbI	..	11.0	11

We shall use the following values of N for ions with the structures indicated: He, 5; Ne, 7; Ar, Cu^+, 9; Kr, Ag^+, 10; Xe, Au^+, 12. Averages of these values for the two ions concerned, given in the last column of Table III, are seen to correspond satisfactorily with the experimental results. There is no experimental verification of the values of n assumed for the eighteen-shell ions. The radii calculated with these values of n from the univalent radii R_1 by means of Equation 13 are included in Table II.[13]

At first it seems that the radius of the cuprous ion would be greater than that calculated by assuming it to be similar to argon, potassium ion, etc., and using the appropriate screening constant (for M_{32} M_{33}); for there are ten M_{32} M_{33} electrons, and only six M_{21} M_{22}. However, the M_{32} M_{33} eigenfunction has its maximum nearer the nucleus than has the M_{21} M_{22} eigenfunction, and the electron density per electron is smaller in the outer part of the atom (corresponding in the old quantum theory to smaller orbital eccentricity). This effect is such that in the outer part of the atom the density of ten M_{32} M_{33} electrons is very nearly equal to that of six M_{21} M_{22} electrons. Accordingly, radii for cuprous ion and similar ions

[11] Born, *Enz. math. Wiss.*, [V] **25,** p. 735.

[12] Herzfeld, "Handbuch der Physik," **1926,** vol. 22, p. 454.

[13] The same results would be obtained by the use of any other function for $\varphi(R)$, instead of the Born expression; for the calculation depends mainly on the first and second derivatives, which are found experimentally.

may be calculated just as though they had the argon structure, but using the M_{32} M_{33} screening constant. Similarly, the silver and the aurous ions may be treated as though they had the krypton and the xenon structure, respectively.

The radii found in this way are given in Table II, the univalent radii being also included, in parentheses. The dependence of the univalent crystal radius and the crystal radius on the atomic number is shown graphically in Fig. 3.[14] The effect of the valence in causing the crystal radius to deviate from the regular dependence on the atomic number shown by the univalent crystal radius is clearly evident.

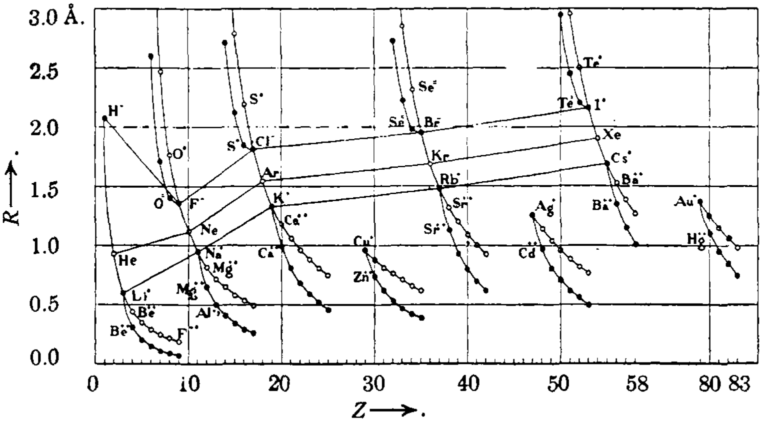

Fig. 3.—The crystal radius (solid circles) and the univalent crystal radius (open circles) for a number of ions.

In deriving theoretical values for inter-ionic distances in ionic crystals the sum of the univalent crystal radii for the two ions should be taken, and corrected by means of Equation 13, with z given a value dependent on the ratio of the Coulomb energy of the crystal to that of a univalent sodium chloride type crystal. Thus, for fluorite the sum of the univalent crystal radii of calcium ion and fluoride ion would be used, corrected by Equation 13 with z placed equal to $\sqrt{2}$, for the Coulomb energy of the fluorite crystal (per ion) is just twice that of the univalent sodium chloride structure. This procedure leads to the result 1.34 Å. (the experimental distance is 1.36 Å.). However, usually it is permissible to use the sodium chloride crystal radius for each ion, that is, to put $z = 2$ for the calcium

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[14] It is to be expected that the relative values of the univalent crystal radius would be of significance with respect to physical properties involving atomic sizes. That this is true for the viscosity of the rare gases is seen from the radii evaluated by Herzfeld (Ref. 12, p. 436) from viscosity data: He, 0.94 (0.93); Ne, 1.18 (1.12); Ar, 1.49 (1.54); Kr, 1.62 (1.69); Xe, 1.77 (1.90). (The values in parentheses are the univalent crystal radii.)

ion and $z = 1$ for the fluoride ion, without introducing a large error; the result 1.35 Å. is obtained in this way for fluorite.[15]

Comparison with Experiment

Empirical Crystal Radii.—A set of crystal radii, derived empirically by Wasastjerna[16] with the aid of mole refraction values, is at present generally accepted[17] as giving satisfactorily the "sizes" of ions in crystals. Wasastjerna's radii are given in Table IV.

TABLE IV

IONIC RADII (WASASTJERNA)

$O^{=}$	1.32 Å.	F^-	1.33 Å.	Na^+	1.01 Å.	Mg^{++}	0.75 Å.
$S^{=}$	1.69	Cl^-	1.72	K^+	1.30	Ca^{++}	1.02
		Br^-	1.92	Rb^+	1.50	Sr^{++}	1.20
		I^-	2.19	Cs^+	1.75	Ba^{++}	1.40

A method for obtaining radii for the alkali and halide ions in agreement with Wasastjerna's was given earlier by Landé,[7c] who assumed the iodide ions in lithium iodide to be in mutual contact. Wasastjerna also pointed out that in some crystals observed inter-atomic distances are explicable with his radii by assuming the anions to be in contact. Bragg and Brown[18] have shown that in a number of oxides the oxygen-oxygen distance is about 2.7 Å., in accordance with a radius of about 1.35 Å.

The radii in Table II are in reasonable agreement with Wasastjerna's, and accordingly also account satisfactorily for the empirical data.

In the past, ionic radii have often been compared with observed inter-atomic distances without much regard to the nature of the crystal from which they were derived. Recently several investigators[19] have concluded that in many crystals the bond between atoms does not consist of the electrostatic attraction of only slightly deformed ions. Goldschmidt in particular has divided crystals into two classes, ionic and atomic crystals, and has shown that ionic radii (using Wasastjerna's set) do not account for the observed inter-atomic distances in atomic crystals. In the following pages our crystal radii will be compared with the experimental dis-

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[15] The forces between ions have been discussed by Lennard-Jones and his collaborators, who have given tables showing the repulsive forces as a function of the repulsion exponent n [Lennard-Jones and Dent, *Proc. Roy. Soc.*, **112A**, 230 (1926)]. In conjunction with Wasastjerna's radii, these tables have been used in the theoretical treatment of crystals such as calcite, $CaCO_3$, which, however, we consider not to be composed of monatomic ions. Thus, they assume C^{+4} and $O^{=}$ to be present in calcite [Lennard-Jones and Dent, *Proc. Roy. Soc.*, **113A**, 673, 690 (1927)], although the carbonate ion is generally believed by chemists to contain shared-electron bonds.

[16] Wasastjerna, *Soc. Sci. Fenn. Comm. Phys. Math.*, **38**, 1 (1923).

[17] For a general discussion see W. L. Bragg, *Phil. Mag.*, **2**, 258 (1926).

[18] Bragg and Brown, *Proc. Roy. Soc.*, **110A**, 34 (1926).

[19] (a) Huggins, *Phys. Rev.*, **21**, 379 (1923); (b) **27**, 286 (1926). (c) Grimm and Sommerfeld, *Z. Physik*, **36**, 36 (1926). (d) Goldschmidt, Ref. 10.

tances in ionic crystals.[20] It will be shown that the theoretical radii account satisfactorily for the experimental results not only for normal crystals, but also for those deviating from additivity (through mutual contact of the anions or through the action of double repulsion), and that furthermore they permit the theoretical prediction of the relative stabilities of the fluorite and the rutile (and anatase) structure, and of the sodium chloride and the sphalerite (and wurzite) structure.

The Alkali Halides.—In Table V are given the experimental inter-atomic distances for the alkali halides with the sodium chloride structure, together with the sum of the radii of Table II.

TABLE V

ALKALI HALIDES WITH THE SODIUM CHLORIDE STRUCTURE

	Li^+, Å.	Na^+, Å.	K^+, Å.	Rb^+, Å.	Cs^+, Å.
H^-, calcd.	2.68				
obs.	2.05				
F^-, calcd.	1.96	(2.31)	2.69	2.84	3.05
obs.	2.01	2.31	2.67	2.82[a]	3.01
Cl^-, calcd.	2.41	2.76	(3.14)	3.29	
obs.	2.57	2.81	3.14	3.29	
Br^-, calcd.	2.55	2.90	3.28	(3.43)	
obs.	2.75	2.97	3.29	3.43	
I^-, calcd.	2.76	3.11	3.49	3.64	
obs.	3.00	3.23	3.53	3.66	

[a] Goldschmidt.

The agreement is satisfactory, except in the cases where there are deviations from additivity. This fact is a verification of our treatment and of the correctness of our screening constants, for the arbitrary selection of only one ionic radius in a series of salts showing additivity in inter-atomic distances is permitted, and our screening constants fixed four radii independently.

The experimental values for the lithium halides are high. This is due to two different phenomena. In the case of the chloride, bromide and iodide the *anions are in mutual contact*, that is, the repulsive forces operative are those between the anions, and the anion radius alone determines the inter-atomic distances. The geometry of the sodium chloride structure requires that, for R_{M^+}/R_{X^-} less than 0.414, the anions come into contact (considering the ions as solid spheres). This requirement is fulfilled for the chloride, bromide and iodide of lithium. In Table VI are given radii

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[20] Huggins, who has particularly emphasized the fact that different atomic radii are required for different crystals, has recently [*Phys. Rev.*, **28**, 1086 (1926)] suggested a set of atomic radii based upon his ideas of the location of electrons in crystals. These radii are essentially for use with crystals in which the atoms are bonded by the sharing of electron pairs, such as diamond, sphalerite, etc.; but he also attempts to include the undoubtedly ionic fluorite and cesium chloride structures in this category.

of these halogen ions calculated from this assumption. The agreement with the calculated radii is satisfactory.

TABLE VI

HALIDE ION RADII IN THE LITHIUM HALIDES

	Obs., Å.	Calcd., Å.
Cl^-	1.82	1.81
Br^-	1.95	1.95
I^-	2.12	2.16

In the case of lithium fluoride the ratio R_{Li^+}/R_{F^-} is 0.44. In this crystal there is *double repulsion;* the repulsive forces between anion and anion and those between anion and cation are simultaneously operative. The inter-atomic distances are determined neither by the sum of the radii for the anion and cation nor by the radius of the anion alone, but are larger than those calculated by either method. Thus the lithium-fluoride distance is 0.05 Å. (2.5%) larger than the sum of the radii, and one-half the fluorine-fluorine distance is 0.06 Å. larger than the fluoride radius.

The sodium salts also show the effect of double repulsion, the increase of the observed distances over the calculated being greatest (2.7%) for the iodide, for which R_{Na^+}/R_{I^-} is 0.44.

The large effect of deformation of the hydride ion, whose mole refraction[6] (deformability) is 25, is shown by the contraction in lithium hydride.

The alkali halides with the cesium chloride structure also show satisfactory agreement, the observed values being about 2.5% larger than the sum of the theoretical radii.

TABLE VII

INTER-ATOMIC DISTANCES FOR CESIUM CHLORIDE TYPE CRYSTALS

	Obs., Å.	Calcd., Å.
CsCl	3.56	3.50
CsBr	3.72	3.64
CsI	3.96	3.85

The Alkaline-Earth Oxides, etc.—The observed and calculated inter-atomic distances for the alkaline-earth oxides, sulfides, selenides and tellurides are given in Table VIII. Except for the magnesium com-

TABLE VIII

ALKALINE-EARTH OXIDES, ETC., WITH THE SODIUM CHLORIDE STRUCTURE

	Mg^{++}, Å.	Ca^{++}, Å.	Sr^{++}, Å.	Ba^{++}, Å.
$O^=$, calcd.	2.05	2.39	2.53	2.75
obs.	2.10	2.40	2.55	2.75
$S^=$, calcd.	2.49	2.83	2.97	3.19
obs.	2.54	2.80[a]	2.94	3.18
$Se^=$, calcd.	2.63	2.97	3.11	3.33
obs.	2.72	2.96	3.12	3.31
$Te^=$, calcd.		3.20	3.34	
obs.		ca. 3.05[a]	ca. 3.24[a]	

[a] Goldschmidt.

pounds, the agreement is excellent, and provides a remarkable verification of our entire procedure, *for the experimental data were in no way involved in the derivation of the theoretical crystal radii.* In magnesium sulfide and selenide the anions are in contact; the radii deduced on this assumption, given in Table IX, are in satisfactory agreement with those calculated.

TABLE IX

THE RADII OF THE SULFIDE AND SELENIDE IONS

	Obs., Å.	Calcd., Å.
$S^=$ (in MgS)	1.80	1.84
$Se^=$ (in MgSe)	1.93	1.98

The ratio $R_{Mg^{++}}/R_{O^=}$ is 0.46, so that in magnesium oxide the mutual repulsion of the oxide ions is beginning to have influence, and the inter-atomic distance is increased by 0.05 Å. (2.5%) through the effect of double repulsion.

Other Binary Compounds.—Scandium nitride and zirconium and titanium carbide do not conform with the theoretical radii. It is possible that these crystals do not consist essentially of Sc^{+3}, N^{-3}, Ti^{+4}, Zr^{+4} and C^{-4} ions, especially since zirconium and titanium nitride, ZrN and TiN, also form crystals with the sodium chloride structure; but possibly also the discrepancy can be attributed to deformation of the anions, which have very high mole refraction values.

TABLE X

NITRIDES AND CARBIDES WITH THE SODIUM CHLORIDE STRUCTURE

	Obs., Å.	Calcd., Å.
ScN	2.22	2.52
TiC	2.15	3.28
ZrC	2.37	3.40

The Fluorite Structure.—In Table XI are given the observed inter-atomic distances in crystals with the fluorite structure. There is good

TABLE XI

INTER-ATOMIC DISTANCES IN FLUORITE TYPE CRYSTALS

		Obs., Å.	Calcd., Å.
CaF_2	Ca^{++}-F^-	2.36	2.35
SrF_2	Sr^{++}-F^-	2.54, 2.51[a]	2.49
BaF_2	Ba^{++}-F^-	2.69	2.71
$SrCl_2$	Sr^{++}-Cl^-	3.03	2.94
Li_2O	Li^+-$O^=$	2.00	(2.00)
Li_2S	Li^+-$S^=$	2.47	2.44
Na_2S	Na^+-$S^=$	2.83	2.79
ZrO_2	Zr^{+4}-$O^=$	2.20	2.20
CeO_2	Ce^{++}-$O^=$	2.34	2.36
Mg_2Si	Mg^{++}-Si^{-4}	2.77	3.35
Mg_2Sn	Mg^{++}-Sn^{-4}	2.94	3.59

[a] Goldschmidt.

agreement in the case of the alkaline-earth halides, except for strontium chloride. Here, however, the large observed value arises from the mutual contact of the chloride ions, which are only 2 × 1.75 Å. apart. The apparently low value 1.75 Å. for the chloride ion radius is due to the fact that in this crystal the Coulomb forces are stronger than in a sodium chloride type crystal, on account of the bivalent cation. We should actually use a theoretical chloride radius obtained by placing $z = \sqrt{2}$, which gives 1.67 Å. The observed value is larger than this, on account of double repulsion.

The agreement is also satisfactory for lithium and sodium sulfide. The oxide was used in calculating the lithium radius, 0.60 Å., for in this compound it is safe to assume that the anions are not in mutual contact. It is further highly pleasing to note that even in zirconium and cerium oxide, containing quadrivalent cations, our theoretical radii are substantiated by the experimental inter-atomic distances; for this makes it probable that even in these crystals the ions are not greatly deformed.

The disagreement found for the compounds magnesium silicide and magnesium stannide may be explained as the result of the deformation of the anions (mole refraction of Si^{-4}, 950; of Sn^{-4}, 228) or, on the other hand, the crystals may not have the ionic structure assumed.

The Rutile Structure.—A large number of compounds MX_2 crystallize with the tetragonal structure of rutile, TiO_2. In this structure the position of the ion X is fixed only by the determination of a variable parameter by means of the intensity of reflection of x-rays from various crystal planes. In accordance with the discussion in a following section, we shall assume the parameter to have the value which causes the distances between X and the three ions M surrounding it to be constant. With this requirement the inter-atomic distance R and the edges a and c of the unit of structure are related by the equation $R = (a/4\sqrt{2})[2 + (c/a)^2]$. In this way the inter-atomic distances in Table XII are obtained. In the case of magnesium fluoride the agreement is satisfactory.

TABLE XII

INTER-ATOMIC DISTANCES IN RUTILE TYPE CRYSTALS AND IN ANATASE

		Obs., Å.	Calcd., Å.
Rutile type MgF_2	Mg^{++}-F^{-}	1.99	2.01
TiO_2	Ti^{+4}-$O^{=}$	1.98	2.08
Anatase type TiO_2[a]	Ti^{+4}-$O^{=}$	1.94	2.08

[a] Vegard, *Phil. Mag.*, **1**, 1151 (1926). Ref. 19 b, p. 638.

Probably the high calculated inter-atomic distances in the oxides are due to our method of using the crystal radii. The substitution in Equation 13 of $z = 4$ for the cation and $z = 2$ for the anion, instead of $z = \sqrt{8}$ for each, would lead to high calculated values in case the anion is much smaller than the cation, as in the rutile type crystals and anatase.

Trivalent Oxides.—It is probable that the rhombohedral crystal corundum, Al_2O_3, consists of ions; that is, the bonds are probably electrostatic. The oxygen ions are arranged in layers parallel to the base (111); within each layer the distances between adjacent ions are 2.50 and 2.89 Å., the values being somewhat uncertain because of the difficulty in the accurate determination of the parameter. These values are probably compatible with the oxygen radius 1.40 Å., calculated for crystals with bivalent cations. The aluminum-oxygen distances are 1.85 and 1.99 Å., in satisfactory agreement with the calculated radius sum 1.90 Å.

Goldschmidt has classed also with the ionic crystals the C-modification of the sesqui-oxides, cubic crystals with 16 M_2O_3 in the unit of structure. The inter-atomic distances reported by him are 2.16–2.20 Å. for scandium oxide and 2.34–2.38 Å. for yttrium oxide, in good agreement with the radius sums 2.21 Å. for Sc^{+3}–$O^{=}$ and 2.33 Å. for Y^{+3}–$O^{=}$.

Eighteen-Shell Ions.—The crystals containing eighteen-shell ions (Table XIII) can be divided into two classes: the first, containing the oxygen or fluoride ion, agreeing reasonably well with the theoretical radii, and the second, containing more easily deformable anions, having smaller inter-atomic distances than the predicted ones. The action of the small cuprous ion on the easily deformable selenium ion (mole refraction, 26.8) is especially large. From these results the conclusion can be drawn that the deforming action of an eighteen-shell ion is much greater than that of an eight-shell ion of the same size and valence. This is to be explained as due to the large effective nuclear charge within the eighteen-shell ions, and it indicates that the deformation of an anion by a cation takes place to a great extent in the interior of the cation, within the outer electron shells.

TABLE XIII

CRYSTALS CONTAINING EIGHTEEN-SHELL IONS

Crystal	Type		Obs., Å.	Calcd., Å.	Δ
CdO	Sodium chloride	Cd^{++}-$O^{=}$	2.36	2.37	0.01
CdF_2	Fluorite	Cd^{++}-F^{-}	2.34	2.33	− .01
HgF	Fluorite	$Hg^{++}F^{-}$	2.43[a]	2.46	.03
ZnF_2	Rutile	Zn^{++}-F^{-}	2.04	2.10	.06
SnO_2	Rutile	Sn^{+4}-$O^{=}$	2.06	2.11	.05
PbO_2	Rutile	Pb^{+4}-$O^{=}$	2.16	2.24	.08
AgF	Sodium chloride	Ag^{+}-F^{-}	2.62[a]	2.63	.00
			(2.46[b]	2.62	.16)
AgCl	Sodium chloride	Ag^{+}-Cl^{-}	2.77	3.07	.30
AgBr	Sodium chloride	Ag^{+}-Br^{-}	2.88	3.21	.33
AgI	Sodium chloride	Ag^{+}-I^{-}	2.99[c]	3.42	.43
Cu_2Se	Fluorite	Cu^{+}-$Se^{=}$	2.49	2.94	.45
TlSb	Cesium chloride	Tl^{+3}-Sb^{-3}	3.33	3.41	.08

[a] From the density φ = 5.852 (Landolt-Börnstein).

[b] Ott, *Z. Krist.*, **63**, 222 (1926).

[c] From solid solutions with silver bromide, Goldschmidt.

Such an action is understandable with the wave-mechanics picture of interpenetrating ions.

It is doubtful that the compound TlSb is to be considered as composed of the ions Tl^{+3} and Sb^{-3}, for much deformation would be expected (the mole refraction of Sb^{-3} is 80), and the inter-atomic distance would then be very much less than the calculated one, instead of only 0.08 Å. less.

Other Crystal Radii.—In Table XIV are collected data from which reasonably accurate crystal radii for some ions not included in Table II may be derived. In all cases fluorides and oxides with the sodium chloride and fluorite structures have been considered to give the correct radius sums. The correction of 2.7% (Ref. 24) was made in selecting the thallous ion crystal radius. The radii derived from rutile type oxides have been

TABLE XIV

EMPIRICALLY DEDUCED CRYSTAL RADII

Crystal	Structure	Obs. distance, Å.	Ion	Effective radius, Å.	Selected radius, Å.
TlCl	Cesium chloride	3.33	Tl^+	1.52	1.44
TlBr	Cesium chloride	3.44		1.49	
TlI	Cesium chloride	3.64[a]		1.48	
MnO	Sodium chloride	2.20	Mn^{++}	0.80	0.80
MnS	Sodium chloride	2.61		.76	
MnF_2	Rutile	2.12[b]		.76	
FeO	Sodium chloride	2.15	Fe^{++}	.75	.75
FeF_2	Rutile	2.06		.71	
CoO	Sodium chloride	2.12	Co^{++}	.72	.72
CoF_2	Rutile	2.04		.68	
NiO	Sodium chloride	2.09	Ni^{++}	.69	.69
NiF_2	Rutile	2.02		.66	
PbF_2	Fluorite	2.57[a]	Pb^{++}	1.21	1.21
PbS	Sodium chloride	2.97[a]		1.13	
PbSe	Sodium chloride	3.03[a]		1.05	
PbTe	Sodium chloride	3.21[a]		1.00	
ThO_2	Fluorite	2.42	Th^{+4}	1.02	1.02
UO_2	Fluorite	2.37	U^{+4}	0.97	0.97
PrO_2	Fluorite	2.32[a]	Pr^{+4}	.92	.92
VO_2	Rutile	1.93	V^{+4}	.53	.59
MnO_2	Rutile	1.84	Mn^{+4}	.44	.50
NbO_2	Rutile	2.01	Nb^{+4}	.61	.67
MoO_2	Rutile	2.00	Mo^{+4}	.60	.66
RuO_2	Rutile	1.97	Ru^{+4}	.57	.63
TeO_2[c]	Rutile	2.21	Te^{+4}	.81	.81
WO_2	Rutile	2.00	W^{+4}	.60	.66
OsO_2	Rutile	1.99	Os^{+4}	.59	.65
IrO_2	Rutile	1.98	Ir^{+4}	.58	.64

[a] Goldschmidt.

[b] The data for rutile type crystals are given in Table XVI.

[c] Because of the anomalous axial ratio of TeO_2 (Table XVI), no attempt was made to correct the radius.

corrected by adding 0.06 Å., derived from the results for tin and lead oxides. Some of these ions, such as Pb^{++}, presumably contain only S electrons and completed sub-groups, and are hence spherically symmetrical. Others, however, deviate from spherical symmetry, so that perhaps one crystal radius alone cannot be assigned each ion.

The effect of deformation is shown in the sulfide, selenide and telluride of lead. Especially interesting is the decrease in the crystal radius in the series Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}; there must then come an increase when the shell is completed, at Zn^{++}, with the radius 0.74 Å.

The Relative Stabilities of Different Ionic Arrangements

The Sodium Chloride and Cesium Chloride Structures.—The agreement found between the observed inter-atomic distances and our calculated ionic radii makes it probable that the crystals considered are built of only slightly deformed ions; it should, then, be possible, with the aid of this conception, to explain the stability of one structure, that of sodium chloride, in the case of most compounds, and of the other, that of cesium chloride, in a few cases, namely, the cesium and thallous halides.

Born[21] has shown that of a number of ionic structures which can be assumed by a binary compound, the sodium chloride arrangement has the lowest Coulomb energy, if it be assumed that the densities of the various forms are the same. He advanced this calculation in explanation of the prevalence of this arrangement in nature. The structures considered were chosen because of the simplicity of their mathematical treatment; no simple arrangement other than the sodium chloride arrangement is included among them, however, so that Born's result is not surprising. As a matter of fact, the Coulomb energy of the sodium chloride arrangement is *greater* than that of one other simple structure (the sphalerite arrangement), assuming the densities of the two forms to be the same. We would expect, however, that not the density, but rather the inter-atomic distance should remain constant for different ionic arrangements. The Coulomb energies of the sodium chloride and cesium chloride structures are[22]

$$\Phi^{(1)}_{\mathrm{NaCl}} = -\,(z^2e^2/R)\;1.7476 \tag{14}$$

$$\Phi^{(1)}_{\mathrm{CoCl}} = -\,(z^2e^2/R)\;1.7624 \tag{15}$$

in which R represents the smallest distance between oppositely charged ions in each case. If this distance were constant, then the Coulomb energy would be smaller for the cesium chloride arrangement, making it more stable than the other.

However, the energy of the repulsive forces must be taken into account; moreover, the possibility of a difference in R in the two structures must

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[21] Born, *Z. Physik*, **7**, 124 (1921).

[22] Emersleben, *Physik. Z.*, **24**, 73, 97 (1923).

be considered. This has been done by Hund[23] who, using the repulsion expression of Equation 8, showed that the cesium chloride structure is stable if the exponent n is greater than 35, and the sodium chloride structure is stable if n is less than 35. This result accounts qualitatively for the observed facts, for from the compressibility data the cesium salts would be supposed to have large values of n; but quantitative agreement is not found.[24] There are a number of possible explanations of the discrepancy. It might be due to the use of the Born repulsive force expression; however, the use of Equation 7, with various reasonable values of m, does not remove the disagreement. The probable explanation is that through deformation of the ions the energy of a crystal is changed somewhat (perhaps by changing the effective charge of the ions slightly, if we consider the deformation to be the attraction of a small portion of the electrons of the anion to a position near the nucleus of the cation), so that the transition occurs at about $n = 12$. It is of interest to mention that this calculation indicates that the crystal energy as calculated by the Born method is accurate only to about 2%, or 4000 cal. per mole.

These considerations also explain the occurrence of cases of dimorphism involving the sodium chloride and cesium chloride structures. It would be expected that increase in thermal agitation of the ions would smooth out the repulsive forces, that is, would decrease the value of the exponent n. Hence the cesium chloride structure would be expected to be stable in the low temperature region, and the sodium chloride structure in the high-temperature region. This result may be tested by comparison with the data for the ammonium halides, if we assume the ammonium ion to approximate closely to spherical symmetry. The low-temperature form of all three salts, ammonium chloride, bromide and iodide, has the cesium chloride structure, and the high-temperature form the sodium chloride structure. Cesium chloride and bromide are also dimorphous, changing into another form (presumably with the sodium chloride structure) at temperatures of about 500°.

The Fluorite and Rutile Structures.—Compounds of the type MX_2 also have their choice of two ionic structures, but the factors influencing them

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[23] Hund, *Z. Physik*, **34**, 833 (1925).

[24] The calculation depends on the difference in the repulsion coefficient β in the two structures, for there are six anion-cation contacts in the sodium chloride structure, and eight in the cesium chloride structure. With $\beta_{NaCl} = 6\beta_0$ and $\beta_{CsCl} = 8\beta_0$, and with $n = 12$, it is found that the equilibrium inter-atomic distance for the cesium chloride structure is about 2.7% greater than that for the sodium chloride structure. For this reason the observed inter-atomic distance in cesium iodide was decreased by this amount in obtaining the initial values for the cesium and iodide crystal radii, which are defined to be valid for a crystal with the sodium chloride structure. It has also been inferred by Goldschmidt, from the observed inter-atomic distances for the two forms of the ammonium halides, that there is a decrease of about 3% in going from the cesium chloride to the sodium chloride arrangement.

in their choice are entirely different from those in the case just considered.[25] The Coulomb energy of the rutile arrangement is a function of two parameters, the axial ratio c/a, and a variable u determining the location of the X ions. We snould expect with spherical ions that the parameter would have the value making the distance between the X ion (3, Fig. 4) and each of the surrounding M ions (A and B) constant, namely

$$u = (1/8)[(c/a)^2 + 2] \qquad (16)$$

This is verified experimentally, except for a small uncertainty; thus, for rutile u should have the value 0.302, corresponding to c/a = 0.644. Vegard[26] gives the experimental value 0.302, Greenwood[27] 0.300 and Huggins[28] 0.30 ± 0.01. Similar agreement is found for other crystals with this structure.

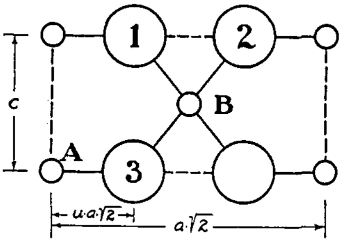

Fig. 4.—Location of titanium ions (small circles) and oxygen ions (large circles) in the plane (110) of rutile.

Bollnow[29] has evaluated the Coulomb energy of the rutile arrangement as a function of the axial ratio c/a, making the assumption that u is given by Equation 16. His results may be given by the equation

$$\Phi^{(1)}_{\text{Rutile}} = -(z^2e^2/R)\alpha \qquad (17)$$

for the Coulomb energy per $M^{+2z}X_2^{-z}$, in which R is the M–X distance, and α has the values given in Table XV. It will be seen that α has a maximum at c/a = 0.721, so that this axial ratio should be assumed by crystals composed of spherical ions, in the absence of disturbing influences. The observed values (Table XVI), except in three cases, lie between the limits 0.62 and 0.71, with an average of 0.67, which is lower than that calculated. The explanation of this (given by Bollnow) is that the X ions 1 and 2 (Fig. 4) are in contact, and so increase a and decrease c/a somewhat; thus the F^-–F^- distance in magnesium fluoride is only 2.57 Å.

TABLE XV

THE COULOMB CONSTANT FOR THE RUTILE STRUCTURE

c/a	u	α	c/a	u	α
0.400	0.27	4.38	0.694	0.310	4.810
.490	.28	4.64	.721	.315	4.816
.565	.29	4.75	.749	.320	4.809
.633	.300	4.783	.800	.330	4.789

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[25] It was shown by Hund (Ref. 23) that for small values of n (less than 6 or 9, depending upon the assumptions made) the rutile structure can become stable. However, our discussion makes it probable that the transition is actually due to the radius ratio.

[26] Vegard, *Phil. Mag.*, **1,** 1151 (1926).

[27] Greenwood, *ibid.*, **48,** 654 (1924).

[28] Huggins, *Phys. Rev.*, **27,** 638 (1926).

[29] Bollnow, *Z. Physik,* **33,** 741 (1925).

TABLE XVI

CRYSTALS WITH THE RUTILE STRUCTURE

Crystal	a, Å.	c, Å.	c/a	Crystal	a, Å.	c, Å.	c/a
MgF_2[a]	4.66	3.08	0.660	NbO_2[e]	4.77	2.96	.620
MnF_2[b,c]	4.88	3.29	.674	MoO_2[e]	4.86	2.79	.573
FeF_2[b]	4.67	3.30	.706	RuO_2[c]	4.51	3.11	.689
CoF_2[b,e]	4.70	3.19	.679	SnO_2[e]	4.75	3.19	.673
NiF_2[b,e]	4.68	3.10	.663	TeO_2[e]	4.79	3.77	.788
ZnF_2[b,e]	4.72	3.13	.663	WO_2[e]	4.86	2.77	.571
TiO_2[d]	4.58	2.95	.664	OsO_2[e]	4.51	3.19	.707
VO_2[e]	4.54	2.88	.634	IrO_2[e]	4.49	3.14	.700
MnO_2[e,d]	4.41	2.88	.653	PbO_2[e]	4.96	3.39	.683

[a] Buckley and Vernon, *Phil. Mag.*, **49**, 945 (1925).
[b] Ferrari, *Atti accad. Lincei*, [6] **3**, 224, 324 (1926).
[c] Van Arkel, *Rec. trav. chim.*, **45**, 437 (1926).
[d] Huggins, Ref. 20.
[e] Goldschmidt, Ref. 10.

and the $O^=$–$O^=$ distance in rutile itself only 2.53 Å. (These low radii arise from the fact that in these crystals, containing bivalent and quadrivalent cations, the Coulomb forces are larger than in sodium chloride type crystals.) The very low axial ratio 0.57 for the dioxides of molybdenum and tungsten and the high axial ratio 0.79 for tellurium dioxide probably are caused by the cations not having spherical symmetry. It will be noticed that the entire range from 0.57 to 0.79 involves a maximum change in the Coulomb energy of only about 1%.

We may accordingly write for α its value for $c/a = 0.67$, so that the Coulomb energy is

$$\Phi^{(1)}_{\text{Rutile}} = -(z^2e^2/R)\ 4.80 \tag{18}$$

For the fluorite arrangement the Coulomb energy is

$$\Phi^{(1)}_{\text{Fluorite}} = -(z^2e^2/R)\ 5.04 \tag{19}$$

Bollnow also evaluated the Coulomb energy of anatase, the other tetragonal form of titanium dioxide, by again making the assumption of a constant Ti^{+4}–$O^=$ distance in order to fix the value of the parameter. He found this energy to have a minimum value

$$\Phi^{(1)}_{\text{Anatase}} = -(z^2e^2/R)\ 4.80 \tag{20}$$

for an axial ratio 2.62, in satisfactory agreement with the observed value 2.51. With the assumption of a constant Ti^{+4}–$O^=$ distance the parameter in anatase should have the value 0.204, in agreement with the experimental values 0.204 (Vegard) and 0.20 ± 0.01 (Huggins).

The possibility of the existence of two forms of titanium dioxide, rutile and anatase, is evident from the identity of their Coulomb energies; taking the energy of the repulsive forces and of possible deformation into account, it is seen that the choice between the two structures would depend on the thermodynamic environment during crystallization. In the case of different compounds the choice might depend on the repulsion exponent *n;* it is interesting that no compounds other than titanium oxide have the anatase structure.

From Equation 19 we should conclude that all ionic crystals MX_2 would have the fluorite structure, on account of the much smaller Coulomb energy for this arrangement. For a compound $M^{+4}X_2^{=}$, with $R = 2$ Å., the free energy of the fluorite arrangement is 160,000 cal. per mole smaller than that of the rutile or anatase arrangement. This very large difference cannot be counteracted by the possible small differences in the repulsion coefficients β, as occurs in the case of the sodium chloride and cesium chloride structures, nor by the effect of deformation. The transition from the fluorite to the rutile structure actually arises from a geometrical effect, the mutual contact of the large anions, and the factor determining the form to be assumed is the ratio of the radius of the cation to that of the anion. From the geometry of the fluorite arrangement it is seen that for values of the ratio R_M/R_X greater than 0.732, contact occurs between anion and cation (considered as rigid spheres), but for smaller values of this ratio the repulsive forces balancing the Coulomb forces will arise from the anions[30] alone, and that the distance R in Equation 19 will not be $R_M + R_X$, but will correspond instead to $2R_X$, the geometrical relation being $R' = \sqrt{3}R_X$. On the other hand, there is still contact between anion and cation in the rutile arrangement, so that R in Equation 18 is given by $R = R_M + R_X$. Substituting these values of R' and R in Equations 19 and 18, and equating $\Phi^{(1)}_{\text{Fluorite}}$ and $\Phi^{(1)}_{\text{Rutile}}$, it is found that the transition radius ratio is

$$R_M/R_X = [(4.80/5.04)\sqrt{3}] - 1 = 0.65 \qquad (21)$$

We have accordingly shown that *for values of the ratio of the crystal radius of the cation to that of the anion greater than 0.65 the fluorite structure is stable; for values less than 0.65 the rutile structure is stable.*

This theoretical result is completely substantiated by experiment. Goldschmidt,[31] from a study of crystal structure data, observed that the radius ratio is large for fluorite type crystals, and small for those of the rutile type, and concluded as an empirical rule that this ratio is the determining factor in the choice between these structures. Using Wasastjerna's radii he decided on 0.67 as the transition ratio. He also stated that this can be explained as due to anion contact for a radius ratio smaller than about 0.74. With our radii we are able to show an even more satisfactory verification of the theoretical limit. In Table XVII are given values of the radius ratio for a large number of compounds. It is seen that the max-

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[30] In this discussion the formula $M^{+2z}X_2^{-z}$ is assumed; for $M_2^{+z}X^{-2z}$ the words cation and anion must be interchanged.

[31] Goldschmidt, *Skrifter Det. Norske Videnskaps-Akad. Oslo I. Matem.-Naturvid. Klasse,* **1926**, No. 1.

TABLE XVII

THE RADIUS RATIO FOR FLUORITE TYPE AND RUTILE TYPE CRYSTALS

Fluorite type	R_M/R_X	Rutile type	R_M/R_X
Li_2S	3.07	PbO_2	0.59
Li_2O	2.33	MnF_2	.59
$K_2[SnCl_6]$[a]	2.24	TeO_2	.58
Cu_2Se	2.06	FeF_2	.55
Na_2S	1.94	ZnF_2	.54
$[Ni(NH_3)_6]Cl_2$	1.41	CoF_2	.53
$[N(CH_3)_4]_2[PtCl_6]$[b]	1.11	NiF_2	.51
BaF_2	0.98	SnO_2	.51
PbF_2	.86	TiO_2	.49
SrF_2	.83	MgF_2	.48
HgF_2	.81	NbO_2	.48
CaF_2	.73	MoO_2	.47
ThO_2	.73	WO_2	.47
CdF_2	.71	OsO_2	.46
CeO_2	.70	IrO_2	.46
UO_2	.69	RuO_2	.45
PrO_2	.66	VO_2	.42
$SrCl_2$	.63	MnO_2	.36

[a] The radii used for complex ions are: $[SnCl_6]^=$, 2.98 Å.; $[Ni(NH_3)_6]^{++}$, 2.55 Å. $[PtCl_6]^=$, 2.88; $[N(CH_3)_4]^+$, 2.60.

[b] Huggins, *Phys. Rev.*, **27**, 638 (1926).

imum value of the ratio for the rutile structure is 0.59, and the minimum value for the fluorite structure 0.63, in satisfactory agreement with the theoretical limit 0.65.[32]

Goldschmidt predicted from his empirical rule that calcium chloride would not have the fluorite structure, and he states that on investigation he has actually found it not to crystallize in the cubic system. Our theoretical deduction of the transition radius ratio allows us to predict that of the halides of magnesium, calcium, strontium and barium only calcium fluoride, strontium fluoride and chloride, and barium fluoride, chloride,

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[32] In this discussion, two mutually canceling simplifications have been made. For the transition value of the radius ratio the phenomenon of double repulsion causes the inter-atomic distances in fluorite type crystals to be increased somewhat, so that R' is equal to $\sqrt{3}R_X.\delta$, where δ has a value of about 1.05 (found experimentally in strontium chloride). Double repulsion is not operative in rutile type crystals, for which $R = R_M + R_X$. From these equations the transition ratio is found to be $(4.80/5.04)\sqrt{3}\delta - 1 = 0.73$, for $\delta = 1.05$; that is, it is increased 12%. But R_M and R_X in these equations are not the crystal radii, which we have used above, but are the univalent crystal radii multiplied by the constant of Equation 13 with z placed equal to $\sqrt{2}$, for $M^{++}X_2^-$. Hence the univalent crystal radius ratio should be used instead of the crystal radius ratio, which is about 17% smaller (for strontium chloride). Because of its simpler nature the treatment in the text has been presented; it is to be emphasized that the complete agreement with the theoretical transition ratio found in Table XVII is possibly to some extent accidental, for perturbing influences might cause the transition to occur for values a few per cent. higher or lower.

bromide and iodide would have the fluorite structure. Of these all but the last three are known to have this structure, and magnesium fluoride is known to have the rutile structure. The oxides, sulfides, selenides and tellurides of all the alkali metals satisfy the fluorite requirement; of these, lithium oxide and sulfide and sodium sulfide are known to have this structure. It will be of interest to carry on the experimental study of others of these compounds.

The Transition to the Sphalerite Structure.—The oxide, sulfide and selenide of beryllium have neither the sodium chloride nor the cesium chloride structure, but instead the sphalerite or the wurzite structure. The Coulomb energy for the sphalerite arrangement is

$$\Phi^{(1)}_{\text{Sphalerite}} = -(z^2e^2/R)\ 1.640 \tag{22}$$

in which R is the smallest anion-cation distance. The Coulomb energy of the closely similar wurzite arrangement has been found by Hund to be the same, within the limits of accuracy of his calculation. He found for the coefficient 1.641 ± 0.003. Comparing this equation with Equations 14 and 15, we should conclude that compounds with undeformed ions could not assume these structures. Accordingly the observed structures of the beryllium salts have previously been explained by saying that the very small beryllium ion has a large deforming action on the surrounding anions.

However, in the wave-mechanics atomic model, deformation occurs within the outer shell of the cation, and in this region the effective nuclear charge of the beryllium ion is only $4e$, instead of $10e$ for eight-shell cations and $20e$ for eighteen-shell cations. Hence we conclude that the deforming action of the beryllium ion is *less* than that of the magnesium, calcium, etc., ions. The explanation of the sodium chloride-sphalerite transition which we advance is the geometrical one used for the fluorite-rutile transition, and does not involve deformation. When the radius ratio R_M/R_X is less than $\sqrt{2}-1 = 0.414$, mutual contact between the anions occurs in the sodium chloride arrangement, so that R in Equation 14 has the value $R = \sqrt{2}R_X$. R in Equation 26 still has the value $R' = R_M + R_X$. Comparing $\Phi^{(1)}_{\text{NaCl}}$ and $\Phi^{(1)}_{\text{Sphalerite}}$, it is found that *for R_M/R_X greater than $(1.640/1.7476)\sqrt{2}-1 = 0.33$ the sodium chloride arrangement is stable, and for a value of the radius ratio less than 0.33 the sphalerite (or wurzite) arrangement is stable.*[33]

In Table XVIII are given values of the radius ratio for the salts of beryllium, magnesium and calcium (those of barium and strontium, with the sodium chloride structure, also obviously satisfy the radius ratio criterion). It is seen that all of the sodium chloride type crystals containing eight-shell cations have radius ratios greater than the limit 0.33, and the beryl-

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[33] The effect of double repulsion for the sodium chloride structure may raise this limit a few per cent.

TABLE XVIII

THE RADIUS RATIO FOR SODIUM CHLORIDE AND SPHALERITE OR WURZITE TYPE CRYSTALS

Sodium chloride structure	R_M/R_X	Sphalerite or wurzite structure	R_M/R_X
CaO	0.71	BeO	0.22
CaS	.54	BeS	.17
CaSe	.50	BeSe	.16
CaTe	.45	BeTe	.14
MgO	.47		
MgS	.35	ZnO	.53
MgSe	.33	ZnS	.40
		ZnSe	.38
CdO	.69	ZnTe	.34
		CdS	.53
		CdSe	.49
		CdTe	.44
		HgS	.60
		HgSe	.56
		HgTe	.50

lium salts with the sphalerite or wurzite structures have lower values of the radius ratio than this limit. Accordingly, the conclusion is drawn that the beryllium salts may be composed of ions, even though they have the sphalerite and wurzite structures.[34]

The prediction may be made that the still unstudied crystal magnesium telluride, with the radius ratio 0.29, has the sphalerite or wurzite structure rather than the sodium chloride structure.

TABLE XIX

INTER-ATOMIC DISTANCES FOR BERYLLIUM SALTS

	Structure	Obs., Å.	Calcd., Å.
BeO	Wurzite	1.65[a]	1.71
BeS	Sphalerite	2.10[a]	2.15
BeSe	Sphalerite	2.20[a]	2.29
BeTe	Sphalerite	2.40[a]	2.52

[a] Goldschmidt.

The observed inter-atomic distances (Table XIX) for the beryllium salts are somewhat smaller than those calculated. This indicates that there is more deformation in these crystals than in the sodium chloride type crystals, despite the smaller effective nuclear charge of the two-shell cation; and points to the existence of an increased tendency to deformation

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[34] It was concluded by Zachariasen [*Norsk geol. Tidsskrift*, **8**, 189 (1925); *Z. physik. Chem.*, **119**, 201 (1926)] from the intensities of reflection of x-rays that beryllium oxide does not contain Be^{++} and $O^{=}$ ions. However, it has since been shown by Claassen [*ibid.*, **124**, 139 (1926)] and Zachariasen himself [*Z. Physik*, **40**, 637 (1926)] that if the electron distribution of the ions is taken into account, the x-ray measurements are compatible with an ionic structure.

in structures in which the anion is surrounded tetrahedrally by cations; that is, in which an electron pair can be shared with each cation.

The radius ratios for sphalerite and wurzite type crystals with eighteen-shell cations do not conform to our criterion, so that some other influence must be operative. Without doubt this is deformation. Here again it is seen that the tetrahedral structure is particularly favorable to deformation, for the observed $Zn^{++}-O^{=}$ distance (1.93 Å.) is 0.21 Å. shorter than the theoretical one, while in cadmium oxide, with the sodium chloride structure, the difference is only 0.01 Å.

Extension to Complex Ions

Many complex ions, such as NH_4^+, $N(CH_3)_4^+$, $PtCl_6^=$, $Cr(H_2O)_8^{+++}$, etc., are roughly spherical in shape, so that they may be treated as a first approximation as spherical. Crystal radii can then be derived for them from measured inter-atomic distances although, in general, on account of the lack of complete spherical symmetry radii obtained for a given ion from crystals with different structures may show some variation. Moreover, our treatment of the relative stabilities of different structures may also be applied to complex ion crystals; thus the compounds K_2SnCl_6, $Ni(NH_3)_6Cl_2$ and $[N(CH_3)_4]_2PtCl_6$, for example, have the fluorite structure, with the monatomic ions replaced by complex ions and, as shown in Table XVII, their radius ratios fulfil the fluorite requirement. Doubtless in many cases, however, the crystal structure is determined by the shapes of the complex ions.

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Summary

Using an atomic model derived from the wave mechanics of Schrödinger, size-screening constants have been calculated for the electrons in many-electron atoms and ions. After a discussion of the forces between ions, and of the significance of ionic sizes, values of the univalent crystal radius and the crystal radius are derived for a large number of ions with the aid of these screening constants, using as a starting point the observed inter-atomic distances in crystals of sodium fluoride, potassium chloride, rubidium bromide, cesium iodide and lithium oxide. The crystal radius of an ion is defined so that the sum of two radii gives the equilibrium distance in a normal crystal with the sodium chloride structure. The univalent crystal radius is the crystal radius the ion would possess if it were univalent, but otherwise unchanged.

The crystal radii for eight-shell ions are in agreement with the observed inter-atomic distances for normal alkali halide crystals, showing that the

various screening constants are self-consistent. Excellent agreement with experiment is found also for the normal alkaline-earth oxides, sulfides selenides and tellurides with the sodium chloride structure, and for the normal alkaline-earth halides, alkali oxides and sulfides and quadrivalent oxides with the fluorite and rutile structures.

In lithium chloride, bromide and iodide, magnesium sulfide and selenide and strontium chloride the inter-atomic distances depend on the anion radius alone, for the anions are in mutual contact; the observed anion-anion distances agree satisfactorily with the calculated radii. In lithium fluoride, sodium chloride, bromide and iodide and magnesium oxide the observed anion-cation distances are larger than those calculated because of double repulsion; the anions are approaching mutual contact, and the repulsive forces between them as well as those between anion and cation are operative.

In crystals containing eighteen-shell cations and not easily deformable anions (F^-), the agreement between the calculated and observed radii is good; for deformable anions ($O^=$, Cl^-, Br^-, I^-), the observed inter-atomic distances are shorter than those calculated.

The theoretical result is derived that ionic compounds MX_2 will crystallize with the fluorite structure if the radius ratio R_M/R_X is greater than 0.65, and with the rutile (or anatase) structure if it is less. This result is experimentally substantiated.

It is also shown that theoretically a binary compound should have the sphalerite or wurzite structure instead of the sodium chloride structure if the radius ratio is less than 0.33. The oxide, sulfide, selenide and telluride of beryllium conform to this requirement, and are to be considered as ionic crystals. It is found, however, that such "tetrahedral" crystals are particularly apt to show deformation, and it is suggested that this is a tendency of the anion to share an electron pair with each cation.

A brief discussion of crystals containing complex ions is given.

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NOTES

Colloidal Phenomena in Dye Solutions.—A remarkable instance of colloidal behavior was observed during a recent investigation of concentration effects. If an aqueous solution of rosaniline hydrochloride is treated with phenol an addition product, $C_{20}H_{20}N_3Cl.2C_6H_5OH$, is formed which does not differ very greatly from the dye itself in general properties and behavior. If rosaniline base is fused with phenol, however, rosaniline phenolate, $C_{20}H_{20}N_3.C_6H_5O$, is obtained. This phenolate is only slightly soluble in water and its aqueous solutions are extremely colloidal. If a dilute, aqueous solution is diluted with an equal volume of water the resulting