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Ionic compressibilities and ionic radii – systematic trends

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Abstract. Ionic radii and compressibilities have been calculated for a number of monovalent and divalent ions and radicals on the basis of the compressible ion theory. In this theory, the compression energy of an ion is given as a two-parameter function of its radius, $A \exp(-r/\rho)$, the radius and compressibility of the ion being monotonically decreasing functions of the compressing force acting on it. Choosing a standard force reflecting the average environment in the alkali halides, univalent radii and compressibilities have been calculated. This is the first theory to estimate ionic compressibilities. The values show systematic trends among groups of related ions. Anions are found to be significantly more compressible than cations (e.g., the compressibilities of Ca^{++}, K^+, Cl^- and S^{--} are respectively 0·8530, 1·342, 2·952 and 5·150 $\times 10^{-12}$ cm²/ dyne). Multivalent or 'crystal' radii and compressibilities have also been calculated by scaling the standard force by the square of the ionic charge. The calculated ionic radii are closer to experimental values than the classical empirical radii.

Keywords. Ionic crystal; compressibility; ionic radius.

1. Introduction

Ion-dependent properties like ionic radius and ionic polarisability have in the past been used with success to describe the bulk properties of ionic crystals. We have recently extended this idea by introducing the concept of ionic compressibility (Narayan and Ramaseshan 1974; Ramaseshan and Narayan 1976). We consider an ion to be a soft sphere whose size is a function of the compressing force acting on it, so that the ion has an internal energy which is a function of its radius. The repulsion between ions arises purely from the increase in their internal energies when compressed together. In this picture, the interionic repulsion energy per molecule in a binary (A^+B^-) cubic ionic crystal is written in the form

$$W_{\text{rep}}(r, r_+, r_-) = W_+(r, r_+) + W_-(r, r_-), \tag{1}$$

where $W_+(r, r_+)$ and $W_-(r, r_-)$ are the compression energies of a pair of neighbouring positive and negative ions, r_+ and r_- are their 'radii' (which are variables) and r is the interionic distance. The ions are assumed to be in contact and so

$$r = r_+ + r_-. \tag{2}$$

The requirement of equilibrium at the point of contact of the two ions then leads to

$$\partial W_+(r, r_+)/\partial r_+ = \partial W_-(r, r_-)/\partial r_-. \tag{3}$$

Because of the two auxiliary conditions, (2) and (3), W_{rep} is ultimately a function of only the interionic distance r.

We also assume that the energy of compression of an ion is local to the points of contact with its neighbours and so the compression energy of the ion at any radius is directly proportional to the number of its neighbours. Thus equation (1) is modified to

$$W_{rep}(r, r_+, r_-) = n[h_+(r_+) + h_-(r_-)] + n'[h_+(br) + h_-(br)], \tag{4}$$

where n and n' are the number of nearest and next nearest neighbours, $h_+(r_+)$ and $h_-(r_-)$ are the compression energies per contact of the two ions and $2br$ is the distance between next nearest neighbours.

It is clear that (4) can be generalised to any ionic crystal of any crystal symmetry containing any number of ions per molecule. The basic feature of the present approach is that each ion has a particular function $h(r_i)$* which is unique to it and independent of the crystal environment in which the ion is placed. The crystal structure enters the theory only through the numbers n, n' and b.

For quantitative work, the compression energy functions $h(r_i)$ have to be modelled by some simple analytical expression. From various considerations, the form chosen was (Narayan and Ramaseshan 1976)

$$h(r_i) = A \exp(-r_i/\rho) \tag{5}$$

where A and ρ are repulsion parameters associated with the individual ions. These parameters have been refined for a number of ions and radicals (Narayan and Ramaseshan 1976, 1977, 1978) using experimental data (lattice constants and compressibilities at different pressures) of simple ionic crystals containing these ions. It should be reiterated that, in our theory, the parameters A and ρ of an ion are unique to it and completely *independent of the crystal environment*. Due to this, the present approach has many features not present in the earlier theories of ionic repulsion (Tosi 1964 gives a review). Some of the advantages of the present theory are:

(i) A relatively small number of parameters are sufficient to describe the properties of a large number of crystals. For instance, with only 18 parameters, the lattice spacings and compressibilities of all the alkali halides, including their variation with pressure, have been satisfactorily fitted.

(ii) The same parameters of an ion can be used in any crystal of any structure in which the ion occurs. For instance, the parameters of Cl^- ion have been used unchanged in a large number of crystals belonging to five structure types viz., NaCl, CsCl, ZnS, CaF_2 and perovskite.

(iii) The theory has been successfully extended without any alterations to ionic radicals (Narayan and Ramaseshan 1978).

(iv) The lattice spacings and compressibilities of a number of perovskite-like crystals have been satisfactorily calculated (Narayan and Ramaseshan 1978) *without introducing any adjustable parameters*. In fact, in the case of four

*Whereas we use r_+ or r_- for the radius of a cation or an anion, we will use the symbol r_i to represent the ionic radius when the discussion is for a general ion.

crystals, the theory unequivocally predicts an inverse perovskite structure with an interchange of the cations.

(v) The theory directly gives the radii of the constituent ions in a crystal and consequently predicts the variation of the radius of an ion from one crystal to another and with pressure in the same crystal.

(vi) The bulk modulus has been calculated for a large number of crystals for which this information is not available experimentally. These values could be used, where necessary, as a first approximation.

The results of our studies so far seem to indicate that the present theory could be quite useful in crystal physics and chemistry, primarily because of its capacity to make *predictions*. However, we are not in a position to exploit this fully because the repulsion parameters of many important ions, notably trivalent and tetravalent cations, are not available, nor can they be easily determined since there is not enough useful crystal data. One possible approach is to extrapolate and obtain the parameters of the new ions from the properties of the ions already studied. In this paper, we make a beginning by studying the regular trends in the parameters of related ions.

2. Ionic radius and compressibility

We shall concentrate on four families of ions which have been studied fairly well by us *viz.*, the alkaline earth, the alkali, the halogen and the chalcogen ions. This sample should be representative enough to deduce trends in the parameters of ions, both row-wise and column-wise in the periodic table. The parameters A and ρ, themselves, are clearly not the best candidates for the type of systematic studies we contemplate because they do not individually have much physical significance. In the theory, they are always coupled together as in $A \exp(-r_i/\rho)$ (the compression energy of the ion) or $(A/\rho) \exp(-r_i/\rho)$ (the compressing force acting on the surface of the ion) or $(A/\rho^2) \exp(-r_i/\rho)$ (which occurs in the expression for the compressibility of the crystal). In fact, these are the quantities that are fitted to the experimental data in refining the parameters. It would not, therefore, be surprising if A and ρ themselves do not vary systematically. Indeed, this is so as seen in figures 1 and 2, where the A and ρ values of the four families of ions are plotted. It appeared to us that it may be more fruitful to transform A and ρ to two other parameters viz., an ionic radius and an ionic compressibility, and seek out systematic relationships in families of ions in terms of these.

In our approach, there is really no unique radius or compressibility associated with an ion since these quantities vary greatly with the crystal environment of the ion. Both the radius and compressibility of an ion decrease with increase in the compressing force acting on its surface. For instance, the radius and compressibility of Cl^- ion would be greater in NaCl than in $SrCl_2$. In fact, even the change in coordination number say, from 6-fold to 8-fold, is likely to alter the properties of an ion. This has been recognised by those working with the Born theory of ionic crystals (Tosi 1964). When they try to determine parameters such as 'crystal radii', they find an arbitrariness which is usually removed by some extra condition such as requiring the 'crystal radii' of the alkali and the halogen ions to conform as closely as possible to the interionic distances in the alkali halides.

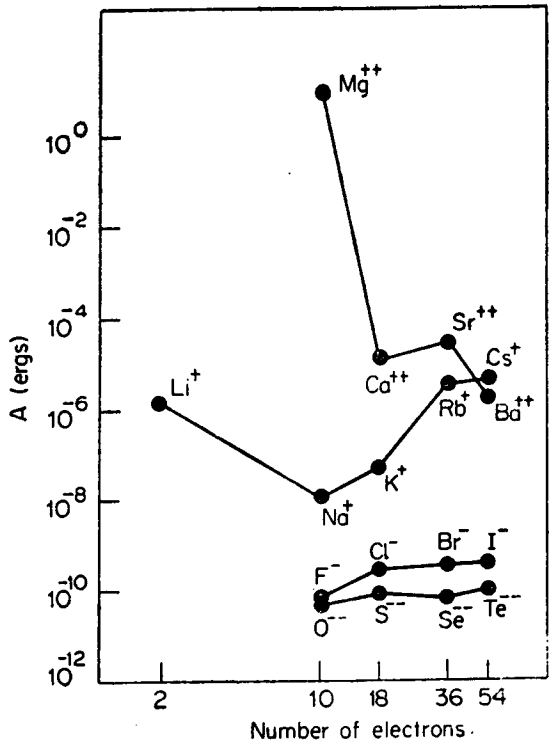

Figure 1. The repulsion parameter A plotted against the number of electrons for some families of ions.

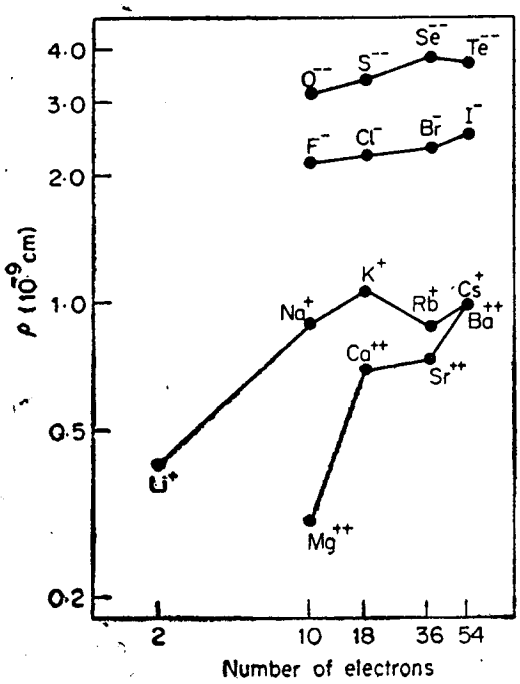

Figure 2. The repulsion parameter ρ plotted against the number of electrons for some families of ions.

We too follow a similar approach. We define a standard environment and define the radius and compressibility of an ion in this environment as the standard values. We choose the standard environment to consist of six forces F acting on the surface of the ion along the cubic directions. The symmetry thus conforms to the environment of an ion in the NaCl lattice. In choosing the magnitude of F, however, we are faced with two options.

(i) We could suitably choose a single value F_0 and calculate the radii and compressibilities of all ions. This would be the most sensible approach for the comparative studies we are attemping here. F_0 may be conveniently chosen as an average of the forces occurring in the alkali halide crystals. In this case, we would calculate what may be termed *univalent* radii and compressibilities (similar to the concept of univalent radius introduced by Pauling 1927, 1960).

(ii) For multivalent ions, the univalent radius and compressibility would be quite different from the ' crystal ' values since the binding in these crystals is much higher. Hence, for estimating crystal properties, it appears better to define *multivalent* radii and compressibilities using $F=v^2F_0$, where v is the valency of the ion (v^2 arising because the compressing force acting on an ion in an ionic crystal is largely due to the Coulomb interaction which is directly proportional to v^2).

Since there are obvious advantages in both approaches, we carry out both analyses in this paper.

3. Univalent radius and compressibility

For calculating the univalent radius and compressibility of an ion, we choose

$$F_0 = 6{\cdot}45 \times 10^{-5} \text{ dyne.} \tag{6}$$

The magnitude of F_0 is so adjusted that the univalent radii calculated for the alkali and halogen ions through equation (8) below give the best possible fit for the interionic spacings in the alkali halides.

From (5), the force F acting on an ion at each contact is given by

$$F(r_t) = (A/\rho) \exp(-r_t/\rho). \tag{7}$$

Equating this to F_0, we have

$$r_u = \rho \ln (A/\rho F_0), \tag{8}$$

where r_u is the univalent ionic radius of the ion. To calculate the compressibility, we first rewrite (7) as

$$r_t = r_u + \rho \ln (F_0/F) . \tag{9}$$

Then, the compressibility K is given by

$$K = -\frac{1}{V}(\partial V/\partial P)_T,$$

$$= (3\,\rho/r_i\,F)\,(dF/dP). \tag{10}$$

Assuming a spherical surface for the ion*, we see that the total force of $6F$ acts on the surface area of $4\pi\,r_i^2$, so that

$$P = (6F/4\pi\,r_i^2),$$

$$\therefore\; dF/dP = 2\pi\,r_i^3/3\,(r_i+2\rho). \tag{11}$$

Substituting in (10), we thus have

$$K_u = 2\pi\,\rho r_u^2/F_0\,(r_u+2\rho), \tag{12}$$

where K_u is the univalent ionic compressibility of the ion.

The pair of numbers r_u and K_u define the properties of an ion as completely as the earlier pair of parameters A and ρ do. To emphasise this, we 'invert' (8) and (12) to obtain A and ρ in terms of r_u and K_u.

$$\rho = K_u\,F_0\,r_u/2\,(\pi\,r_u^2 - K_u\,F_0), \tag{13}$$

$$A = \rho\,F_0\exp\,(r_u/\rho). \tag{14}$$

The advantage of the pair, r_u and K_u, over the earlier pair, A and ρ, is that one can more readily see their physical significance.

4. Trends in r_u and K_u

Table 1 lists the values of r_u and K_u for all the ions we have studied. The values for the four families of ions of particular interest to us are plotted in figure 3 and 4. It is quite significant and gratifying that the new parameters show an improved systematic behaviour compared to A and ρ (figures 1 and 2).

The r_u values of related ions show the following qualitative relationships:

(i) The r_u values of ions belonging to the same column of the periodic table increase with the atomic number.

*This is a crude approximation because, according to the present theory, ions are not spherical. However, this approximation will only introduce a scale factor into the calculated values of compressibility and will not affect the trends which we seek. A later paper (Narayan and Ramaseshan 1979) describes a more detailed theory of ionic crystals in which the shapes of ions are also taken into account.

Table 1. Repulsion parameters, univalent radius and univalent compressibility of ions and radicals studied with the present theory.

Ion	v	A (erg)	ρ (Å)	r_u (Å)	K_u (10^{-12} cm²/dyne)
Li^+	1	$0{\cdot}1544 \times 10^{-5}$	0·04158	0·7430	0·2706
Na^+	1	$0{\cdot}1211 \times 10^{-7}$	0·09029	1·106	0·8359
K^+	1	$0{\cdot}5600 \times 10^{-7}$	0·1078	1·466	1·342
Rb^+	1	$0{\cdot}3980 \times 10^{-5}$	0·08883	1·604	1·250
Cs^+	1	$0{\cdot}5604 \times 10^{-5}$	0·09977	1·824	1·598
Cu^+	1	$0{\cdot}1222 \times 10^{+13}$	0·01542	0·9263	0·1347
Ag^+	1	$0{\cdot}3404 \times 10^{-3}$	0·05481	1·260	0·6189
Tl^+	1	$0{\cdot}7386 \times 10^{-6}$	0·1001	1·627	1·413
F^-	1	$0{\cdot}7506 \times 10^{-10}$	0·2152	1·354	2·154
Cl^-	1	$0{\cdot}2958 \times 10^{-9}$	0·2240	1·708	2·952
Br^-	1	$0{\cdot}3724 \times 10^{-9}$	0·2352	1·836	3·348
I^-	1	$0{\cdot}4407 \times 10^{-9}$	0·2538	2·005	3·955
H^-	1	$0{\cdot}1604 \times 10^{-10}$	0·3150	1·376	2·897
Mg^{++}	2	$0{\cdot}9939 \times 10^{+1}$	0·03051	1·033	0·2899
Ca^{++}	2	$0{\cdot}1471 \times 10^{-4}$	0·07017	1·375	0·8530
Sr^{++}	2	$0{\cdot}3483 \times 10^{-4}$	0·07441	1·518	1·002
Ba^{++}	2	$0{\cdot}1997 \times 10^{-5}$	0·09919	1·712	1·482
Zn^{++}	2	$0{\cdot}1562 \times 10^{-2}$	0·04713	1·162	0·4936
Cd^{++}	2	$0{\cdot}3410 \times 10^{-5}$	0·07645	1·380	0·9253
Hg^{++}	2	$0{\cdot}6079 \times 10^{+23}$	0·01680	1·422	0·2273
Mn^{++}	2	$0{\cdot}2941 \times 10^{+13}$	0·01733	1·054	0·1723
Fe^{++}	2	$0{\cdot}7895 \times 10^{+15}$	0·01515	1·008	0·1445
Co^{++}	2	$0{\cdot}9939 \times 10^{+11}$	0·01737	0·9978	0·1632
Ni^{++}	2	$0{\cdot}1251 \times 10^{+12}$	0·01656	0·9559	0·1490
Sm^{++}	2	$0{\cdot}3309 \times 10^{+3}$	0·04081	1·513	0·5706
Eu^{++}	2	$0{\cdot}3412 \times 10^{+6}$	0·03370	1·490	0·4678
Yb^{++}	2	$0{\cdot}1104 \times 10^{+8}$	0·02944	1·408	0·3875
Pb^{++}	2	$0{\cdot}2814 \times 10^{-4}$	0·08014	1·612	1·145
O^{--}	2	$0{\cdot}5135 \times 10^{-10}$	0·3160	1·747	3·950
S^{--}	2	$0{\cdot}8843 \times 10^{-10}$	0·3431	2·055	5·150
Se^{--}	2	$0{\cdot}6948 \times 10^{-10}$	0·3877	2·182	6·079
Te^{--}	2	$0{\cdot}1071 \times 10^{-9}$	0·3771	2·296	6·347
NH_4^+	1	$0{\cdot}1698 \times 10^{-4}$	0·07820	1·535	1·062
SH^-	1	$0{\cdot}1759 \times 10^{-7}$	0·1545	1·867	2·410
SeH^-	1	$0{\cdot}1463 \times 10^{-5}$	0·1190	1·995	2·066
CN^-	1	$0{\cdot}3460 \times 10^{-9}$	0·2288	1·775	3·146
NH_2^-	1	$0{\cdot}9310 \times 10^{-7}$	0·1149	1·614	1·581
ClO_3^-	1	$0{\cdot}4614 \times 10^{-5}$	0·1186	2·125	2·208
BrO_3^-	1	$0{\cdot}5821 \times 10^{-5}$	0·1200	2·176	2·291
ClO_4^-	1	$0{\cdot}3489 \times 10^{-9}$	0·2724	2·069	4.345
BH_4^-	1	$0{\cdot}1294 \times 10^{-9}$	0·2682	1·775	3·561
BF_4^-	1	0.2959×10^{-4}	0·1068	2·123	2·007
NO_3^-	1	$0{\cdot}5882 \times 10^{-9}$	0·2354	1·945	3·591
SO_4^{--}	2	$0{\cdot}7213 \times 10^{-9}$	0·2838	2·350	5·232
NH^{--}	2	$0{\cdot}3258 \times 10^{-10}$	0·3954	1·918	5·230

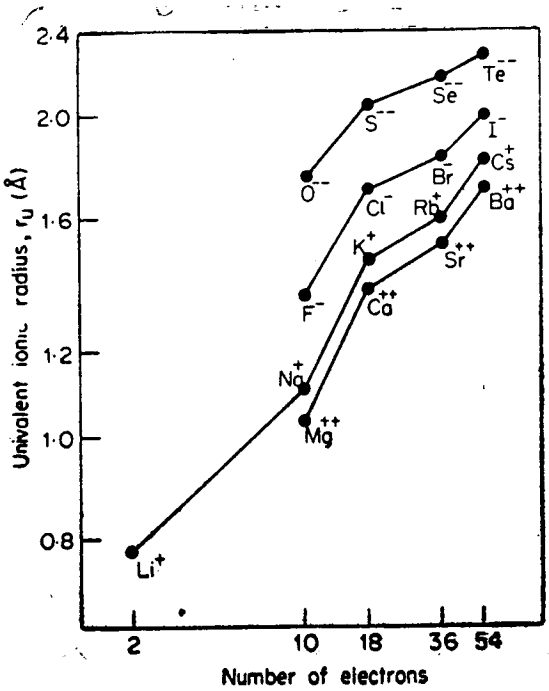

Figure 3. The univalent radius r_u of some ions plotted against the number of electrons.

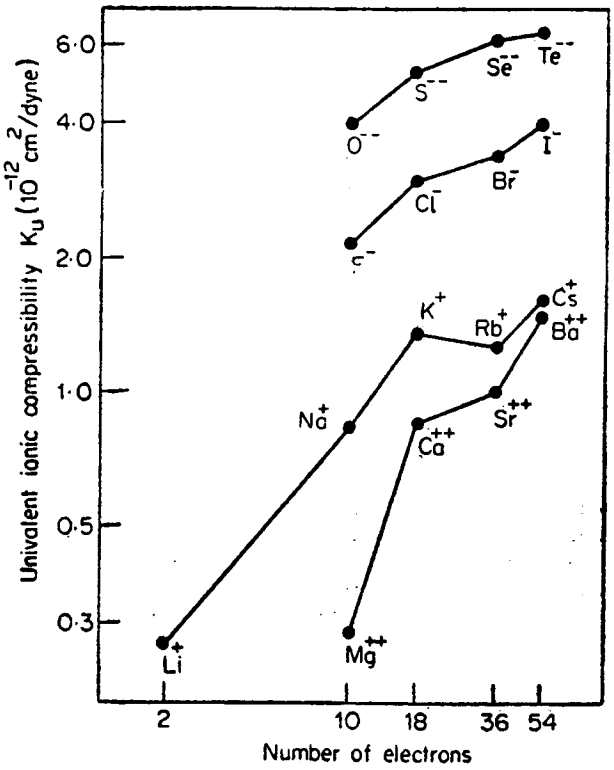

Figure 4. The univalent compressibility K_u of some ions plotted against the number of electrons.

(ii) The r_u values of equi-electronic ions increase rapidly with decrease in the atomic number (e.g., the sequence Ca^{++}, K^+, Cl^-, S^{--}).
(iii) The r_u values of divalent ions of transition and rare-earth elements decrease with increase in atomic number.
(iv) Anions are generally larger than cations and so determine, to a large extent, the structure of crystals.

Similar generalisations to those made above have been made before (e.g. Evans 1966) with regard to the classical crystal radii. It is satisfying that our univalent radii reproduce the same systematic trends.

Ionic *compressibility*, however, is a *new concept* that we have introduced and this is probably the first time estimates of this quantity have been obtained for various ions. The K_u values of related ions show the following remarkable qualitative relationships:

(i) The K_u values of ions belonging to the same column of the periodic table increase with the atomic number.
(ii) The K_u values of equi-electronic ions increase rapidly with decrease in the atomic number.
(iii) The K_u values of the divalent rare-earth ions decrease with increase in atomic number (the results in the case of transition metal ions are inconclusive).
(iv) Anions are generally very much more compressible than cations and so determine, to a large extent, the compressibility of the crystal.

These are only qualitative statements but they fit very well with our intuitive ideas of ionic compressibility. We are currently attempting to quantify the above relationships so that extrapolations could possibly be made to other ions.

Apart from extrapolations to other ions, we point out another interesting possibility. In figures 3 and 4, we see four lines corresponding to ions of charge +2, +1, −1 and −2. Surely, there must be another line in the middle corresponding to 0 charge which would include the rare gases Ne, Ar, Kr and Xe. It would be interesting to estimate r_u and K_u for these atoms from figures 3 and 4 and see how well they *predict* the properties of the rare gas crystals. Calculations along these lines are currently being carried out.

5. Multivalent ionic radius and compressibility

For calculating the multivalent radius and compressibility of ions, we follow the second option discussed in § 2 and take $F = v^2 F_0$, where v is the valency of the ion and F_0 is given by (6). We then obtain the following relations

$$r_m = \rho \ln (A/\rho\, v^2 F_0), \tag{15}$$

$$K_m = 2\pi \rho\, r_m^2/v^2 F_0 (r_m + 2\rho), \tag{16}$$

where r_m and K_m are the multivalent radius and compressibility of the ion. For multi-

valent ions, the quantities r_m and K_m rather than r_u and K_u are suitable for estimating their crystal properties.

Table 2 lists r_m and K_m for the various divalent ions we have studied (for the monovalent ions, $r_m = r_u$ and $K_m = K_u$). One notices that the multivalent radii of the divalent ions are approximately equal to the r_u values of the equivalent monovalent ions. This implies that the lattice spacings of monovalent and divalent ion crystals are approximately equal. Secondly, considering the K_m values, one notices that the anions are much more compressible than the cations and so are primarily responsible for the compressibility of the divalent ion crystals. Since the K_m values of the chalcogen ions are about three times smaller than those of the halogens, the divalent ion crystals are on the average three times less compressible than the monovalent ion crystals. The remarkable fact is that the chalcogen ions are, intrinsically, almost twice as compressible as the halogen ions (compare their K_u values in table 1). Their compressibilities are reduced by a factor of about six when the compressing force increases from F_0 to 4 F_0. This illustrates the fact that the compressibilities of ions (as also their radii) vary strongly with their environment.

6. Comparison of univalent and multivalent radii with classical ionic radii

Estimates of the radii of ions have been made by a number of authors (Pauling 1960; Goldschmidt 1926; Zachariasen 1956; Shannon 1976) based on the requirement that

Table 2. Multivalent radii and compressibilities of divalent ions and radicals.

Ion	v	r_m (Å)	K_m (10^{-12} cm²/dyne)
Mg^{++}	2	0·9906	0·06934
Ca^{++}	2	1·278	0·1968
Sr^{++}	2	1·415	0·2320
Ba^{++}	2	1·574	0·3377
Zn^{++}	2	1·097	0·1159
Cd^{++}	2	1·274	0·2118
Hg^{++}	2	1·398	0·05587
Mn^{++}	2	1·030	0·04207
Fe^{++}	2	0·9874	0·03535
Co^{++}	2	0·9737	0·03977
Ni^{++}	2	0·9329	0·03633
Sm^{++}	2	1·456	0·1371
Eu^{++}	2	1·443	0·1131
Yb^{++}	2	1·367	0·09395
Pb^{++}	2	1·501	0·2647
O^{--}	2	1·309	0·6795
S^{--}	2	1·580	0·9202
Se^{--}	2	1·644	1·055
Te^{--}	2	1·773	1·142
SO_4^{--}	2	1·956	1·048
NH^{--}	2	1·370	0·8361

the ionic radii should add up approximately to the interionic spacings in crystals. It would be interesting to compare a typical set of these radii with the univalent and multivalent radii calculated in this paper.

The univalent radii of Pauling (1960) are compared with our r_u values in table 3. Our r_u values are larger than those of Pauling's for the cations and smaller for the anions. It is not possible to resolve the question as to which of the two sets is closer to reality since the actual radii of ions are generally not known in ionic crystals. In a few crystals, electron density distributions have been obtained by x-ray methods. In NaCl (Witte and Wolfel 1958; Schoknecht 1960) the electron density suggests a

Table 3. Univalent radii (in Å) as given by Pauling (upper lines) and the present theory (lower lines).

	H^-	Li^+	Be^{++}
	2·08	0·60	0·31
	1·376	0·743	—
O^{--}	F^-	Na^+	Mg^{++}
1·76	1·36	0·95	0·82
1·747	1·354	1·106	1·033
S^{--}	Cl^-	K^+	Ca^{++}
2·19	1·81	1·33	1·18
2·055	1·708	1·466	1·375
Se^{--}	Br^-	Rb^+	Sr^{++}
2·32	1·95	1·48	1·32
2·182	1·836	1·604	1·518
Te^{--}	I^-	Cs^+	Ba^{++}
2·50	2·16	1·69	1·53
2·296	2·005	1·824	1·712

Table 4. Crystal radii (in Å) as given by Pauling (upper lines) and the present theory (lower lines).

	H^-	Li^+	Be^{++}
	2·08	0·60	0·31
	1·376	0·743	—
O^{--}	F^-	Na^+	Mg^{++}
1·40	1·36	0·95	0·65
1·309	1·354	1·106	0·991
S^{--}	Cl^-	K^+	Ca^{++}
1·84	1·81	1·33	0·99
1·580	1·708	1·466	1·278
Se^{--}	Br^-	Rb^+	Sr^{++}
1·98	1·95	1·48	1·13
1·644	1·836	1·604	1·415
Te^{--}	I^-	Cs^+	Ba^{++}
2·21	2·16	1·69	1·35
1·773	2·005	1·824	1·574

radius of 1·17 Å for Na^+ and 1·65 Å for Cl^-. Our r_u values are closer to these numbers than those of Pauling's radii.

We compare our multivalent radii r_m with those of Pauling in table 4 (the ionic radii of most of the other authors mentioned above are closely related to Pauling's multivalent radii). The striking feature of table 4 is that the opposing shifts in the radii of the cations and anions are very much more pronounced here. This occurs because the two methods of calculation are different. Pauling's approach is one of *equal compressibility* by which he scales down all the radii by approximately a constant factor. In our theory, on the other hand, the difference between the r_m and r_u values of an ion *depends on its compressibility*, which is large for an anion and small for a cation. Thus, for the anions, we predict a large change from r_u to r_m whereas, for the cations, the changes are much smaller. The comparatively large polarisabilities of anions seem to favour our picture of soft anions and much harder cations as against Pauling's 'equi-compressible ions'.

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