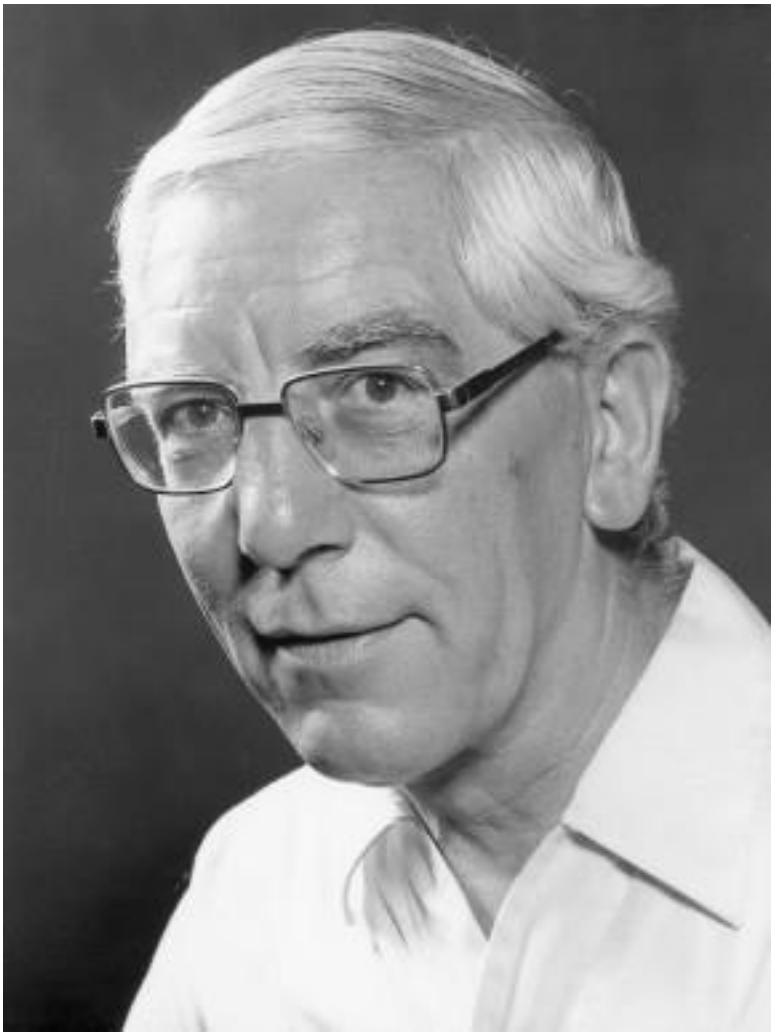
Liversidge Research Lecture

No. 25
1986

INORGANIC AND MINERAL STRUCTURES RECONSIDERED

B. G. HYDE

The Royal Society of New South Wales



Bruce Godfrey Hyde

Liversidge Research Lecturer No. 25, 1986.

BRUCE GODFREY HYDE 1925-2014

Bruce Godfrey Hyde was born on 13 March 1925 at Abercynon (Glamorgan, South Wales). His secondary education was at Newton Abbot Grammar School (Devon, UK). After two years as a chemist at the Newton Abbot Gas Company Gas Co. (Newton Abbot, Devon), and four years in the Royal Navy, he proceeded to Bristol University (UK), graduating B.Sc.(Hons.IIA) in 1951. He then worked under Dr. W.J. Dunning on the *Thermodynamics of Aqueous Sucrose Solutions* (but did not submit his thesis until 1961, graduating Ph.D. in 1962. He was a 'Postdoctoral' Fellow at the Chemistry Department, University of Melbourne from 1954 to 1957, and Lecturer in Physical Chemistry in that Department from 1957 to 1960. He then went to the Chemistry Department, of the State University of Iowa (USA) as Visiting Lecturer during 1960-1961, and from 1962 to 1964 he was Senior Research Fellow in the Chemistry Department of Arizona State University (USA): in both of these places he worked with LeRoy Eyring. In 1964 he was appointed Senior Lecturer in Inorganic Chemistry at the University of Western Australia; promoted to Reader in 1968, and to a Personal Chair in 1975. For the period 1975-1977 he held the Chair of Inorganic Chemistry at the Gorlaeus Laboratory in the University of Leiden (The Netherlands), but then resumed his position in the University of Western Australia. This he relinquished at the end of 1978 to take up a Chair of Inorganic Chemistry at the Research School of Chemistry, Australian National University from 1979 until his retirement in 1990 (when he was appointed Emeritus Professor).

Since 1954, Bruce Hyde's main research interest has been in inorganic solid-state chemistry, first in the thermodynamics of "nonstoichiometric systems" ($PrO_x + O_2$, $TbO_x + O_2$; $TiO_x + O_2$). This interest was later extended to the crystal chemistry of titanium (and other) oxides - mainly studied by electron microscopy - and then to crystal structures in general. His interest in 'the defect solid state' was originally stimulated by his period of work with J.S. Anderson (in Melbourne) in the 1950s. Later - working on rare earth oxides with LeRoy Eyring (at Arizona State University) and 'Judge' Bevan (there and, later, at the University of western Australia) - he departed from traditional (classical) ideas of 'defects' to the more satisfactory notions of David Wadsley and Sten Andersson. Ideas on crsytal chemistry in general have been especially developed during collaborations with Sten Andersson and Michael O'Keeffe.

Honours and Awards (Pre 2001)

1975 FAA

1976 H.G. Smith Medal, Royal Australian Chemical Institute (RACI)

1977 FRACI

1986 Liversidge Research Lecture, Royal Society of New South Wales

1992 Australian Journal of Chemistry Volume **45**(9), "Issue Dedicated to Bruce Hyde"

199?- Honorary Life Member, RACI.

Biographical Source

Personal communication

Because Bruce Hyde was a Fellow of the Australian Academy of Science (FAA), a detailed biographical memoir will be published in *Historical Records of Australian Science*, in due course.

Scientific Publications by B.G. Hyde

Between 1965 and 1996 B.G. Hyde published 123 papers on inorganic chemistry, and 3 monographs. He has written a manuscript "David Wadsley: scientific life and letters", that is yet to be published.

INORGANIC AND MINERAL STRUCTURES RECONSIDERED*

B. G. HYDE
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ABSTRACT. For 60 years or so the "Ionic Model" has been fundamental to solid state chemistry and mineralogy. It has been useful, but the ideas involved have become sacrosanct, even when they do not work! Quantum mechanical methods are becoming increasingly important and useful, but they lack the simple "physical" approach and, in any case, so far can only be applied to the simpler structures.

An alternative approach, as simple, naive and "physical" as the ionic model, is successful where the latter succeeds and where it fails (e.g. in silicates). It can often be useful for simple and complicated structures; and it avoids the ionic/covalent dichotomy. Like the successful quantum methods, it sees no difference in principle between non-molecular structures and those of small molecules (another unhappy dichotomy). It emphasises that, as in organic chemistry, one "size" for an atom is insufficient for understanding structure; at the crudest level one needs a bonding size (for first nearest neighbour interactions) and a non-bonding size (for second and further neighbours).

The usefulness of this alternative approach is demonstrated in several areas of interest, particularly to the chemist and mineralogist: in (a) determining crystal structures and coordination numbers therein, (b) its effect on the stability/instability (and even non-existence) of simple compounds such as binary oxides, nitrides and carbides, (c) leading to simple descriptions of the structures of some mundane compounds such as sulphates, silicates and carbonates, previously undescribed, but (d) often of interest to physicists because their structures may be incommensurably modulated, (e) accounting for the effect of high pressure on crystal structure.

It transpires that cations, far from being small in size and influence, often dominate crystal structure and behaviour.

Preface

It is an honour to have been invited by the Royal Society of New South Wales to give its Liversidge Research Lecture for 1986. I note that is the twenty-fifth such lecture, and that today - September 24th, 1986 - is exactly the fifty-fifth anniversary of the first.

What I have to say is, I believe, consistent with the wishes of Archibald Liversidge - to stimulate the acquisition of knowledge by research. At the early age of 20 he was awarded medals in mineralogy, chemistry and metallurgy, all of which are germane to my theme; and whose structural aspects have been my preoccupation for a number of years. Liversidge was admonished for not being sufficiently interested in the crystallographic aspects of mineralogy but, it should be pointed out, he retired from his Sydney University Chair five years before Friedrich and Knipping's crucial experiment on the diffraction of X-rays by crystals (in 1912).

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*Liversidge Research Lecture delivered before the Royal Society of New South Wales, September 24th, 1986, at The University of Sydney. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1986, **119**, 153-164.

Nevertheless, as is appropriate (for it has long been a strong field of endeavour in this country) crystal chemistry has figured prominently among the Liversidge Lectures: Stuart Anderson (1942), Lloyd Rees (1952), Ray Martin (1976) and, in somewhat different veins, Hans Freeman (1978) and David Craig (1982). But I would especially wish to recall the late David Wadsley (Figure 1), whose 1958 Liversidge Lecture on "Modern Structural Inorganic Chemistry" (A.D. Wadsley, 1958) was a significant part of his transformation of our appreciation of crystal structures, particularly of inorganic compounds and minerals. During his lecture he pointed out that inorganic chemistry had its origins in mineralogy and "still continues to draw upon minerals as the raw material for study." I can only reiterate that: it links my lecture with Wadsley's, and with Liversidge himself since, in 1880, he was appointed Professor of Chemistry and Mineralogy in the University of Sydney.

Introduction

The two main facets of crystal chemistry (the science of non-molecular crystal structures) are *description* and *explanation.* The first has a long history (stemming from Goldschmidt, Bragg and Pauling, 50-60 years ago), revolutionised by Wadsley. It now seems to have matured; with the emphasis shifting towards other types of structures, e.g. quasi-crystals and glasses. The second, aimed at trying to understand why a compound has the structure it has and not some other that seems equally (or even more) plausible; and at trying to understand why, with say changing temperature or (especially) pressure, it transforms to a new structure, is not as advanced. It is an active field of research, now developing rapidly in new directions - particularly by the application of quantum mechanics (see, for example, M. O'Keeffe and A. Navrotsky, 1981). It is clearly of concern to fundamental and applied science, and underlies our understanding of mechanisms of solid state (i.e. most) reactions.

FIGURE 1. David Wadsley, 1918 - 1969.

Quantum methods are very powerful and successful, but cannot yet handle complex structures. In any case there is a need for a simpler, intuitive approach - with some "physical" feel; and this is what Professor Michael O'Keeffe (of Arizona State University) and I have been attempting to develop in the last few years. It involves a reassessment of

the accepted "truth", i.e. the Ionic Model, and a review of at least a part of simple inorganic chemistry, such as the binary and ternary oxides of the Group I elements.

A complete treatment cannot be brief; and so I will consider only a few pieces of the jigsaw which is, in any case, still incomplete. Some reconsideration of the old is followed by some consideration of the new.

The Ionic Model

The sodium chloride structure, shown in Figure 2 (W. Barlow, 1898), is described as a virtually infinite array of Na^+ and Cl^- ions. It perfectly exemplifies the ionic model, which has been the basis on which non-molecular crystal structures have been described and understood (and misunderstood) for over 60 years. In its simplest terms this employs *"close-packed"* arrays of (negative) anions (cf. Figure 3) - Cl^- in the case of NaCl - into which (positive) cations are inserted in appropriate interstices, commonly octahedral (as in NaCl) or tetrahedral. The appropriateness is said to be determined by the radius ratio $\rangle$ = (cation radius) / (anion radius): $\geq$ 0.225 for cation coordination number (C.N.) = 4, $\geq$ 0.414 for C.N. = 6, $\geq$ 0.732 for C.N. = 8, and so on.

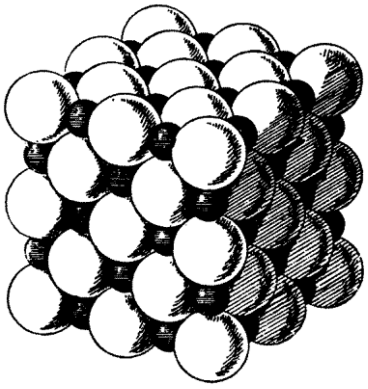

FIGURE 2. The structure of NaCl as a composite of Na and Cl atoms or ions (W. Barlow, 1898)

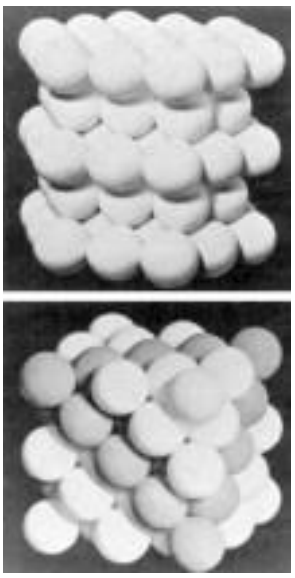

FIGURE 3. The two simplest forms of close-packing, (a) hexagonal, (b) cubic

Even though it sometimes works (those cases beloved by text-book authors!), I believe it to be fundamentally wrong. This assertion is justified by making a few simple points:

1. Consider the series of Group II oxides (MgO to BaO), all of which have this NaCl-type structure. The (oxide) anions cannot be close packed in every case because there is a large range of distances involved: nearest-neighbour oxygen-oxygen distances, *d*(O...O) = 2.98 Å in MgO up to 3.91 Å in BaO. Indeed, BaO, SrO and, possibly, CaO all violate the radius ratio rule.

2. It transpires that the geometry of *close*-packing is also the geometry of *open*-packing (G.O. Brunner, 1971; M. O'Keeffe, 1977). The latter allows anion-anion and cation-cation distances to be a maximum (not minimum) subject to the constraint of a given bond length (i.e. cation-anion distance). Clearly, open-packing is more reasonable for *ion* arrays: it minimises electrostatic energy. Hence, some people now use the term "arranged as in close-packing", for which circumlocution we prefer the neutral term "eutactic" = well arranged (M. O'Keeffe, 1977).

3. Many structures have anion arrays that are not even regular, let alone "close-packed" or eutactic. Their geometries are then very difficult, and often impossible, to describe in the conventional terms of the geometry of their anion arrays, or the articulation of their cation-centred polyhedra of anions. But, as we shall see, in many of these cases the cation array is regular, and its geometry familiar.

4. Radius ratio and coordination numbers are often not related by the "radius ratio" rule (cf. above). For example:
   a . ^{V1}Mg in MgO, but ^{IV}Mg in $MgAl_2O_4$ (spinel)*

   b. in $^{IV}Mg^{VI}Al_2{}^{IV}O_4$ the larger cation (Mg^{2+}, r = 0.71/0.57 Å)** is in the smaller, tetrahedral interstice in an almost eutactic array of oxygens, but the smaller cation (Al^{3+}, r = 0.675/0.535 Å) is in the larger, octahedral hole.

   c. There are ternary compounds of alkali and transition metal oxides in which various coordination numbers are observed for a given cation, particularly for the alkali metals, e.g. Na whose C.N. ranges from 2 to 12! (R.D. Hoppe, 1980).

5. Calculated (and accurate) electron density maps of MgO (M.S.T. Bukowinski, 1982) show a minimum density along the line Mg-O at 0.91 Å from Mg. Such a minimum is often taken to indicate the dividing surface between cation and anion and, if the density is integrated one finds that a sphere of this radius centred on Mg includes a net charge of +1.9 e. But the tangent sphere about the O nucleus includes a charge of only -0.9 e. This means that 1.0 electrons (per MgO) are "in the cracks", between such spheres.

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* The coordination number of atom is denoted by a preceding, Roman numeral superscript.

** The two values of the cation radii are first the more recent value of Shannon (1976), stemming from Fumi and Tosi (1964), and second the classical value of Pauling (1960).

6. The size of an Si^{4+} ion is accepted as 0.40/0.26 Å for C.N.(Si) = 4. But, if we (reasonably) define its size as the radius of the sphere about the nucleus of a neutral atom that contains 10 electrons then, using the SCF orbital wave functions of Clementi and Roetti (1974), we get a value of 0.61 Å. This is consistent with the experimental value of 0.58 Å for Si^{4+} in ⟨-quartz (R.F. Stewart, M. Spackman, 1981), but completely inconsistent with the accepted ion radius of 0.40/0.26 Å (for 4-coordination).

The conclusion is that the ionic model cannot survive close scrutiny, and so we look to an alternative.

The Alternative Approach

This treats atoms simply as atoms although, we retain the terms cation and anion to distinguish metal from non-metal atoms. It is a simple approach that may be (although it was not) logically developed from an observation made some years ago by Bragg and Claringbull in their important book "The Crystal Structures of Minerals" (L. Bragg, G.F. Claringbull, 1965). Discussing the related structures of the three pyroxene minerals diopside ($Ca_{1/2}Mg_{1/2}SiO_3$), pigeonite ($(Ca,Mg,Fe)SiO_3$) and clinoenstatite ($MgSiO_3$) , they observed that all had SiO_3 chains of corner-connected SiO_4 tetrahedra, and that there were five different conformations of these chains, Figure 4. They pointed out that "The Si-Si distance in a single chain, 3.05 Å, is the same in all three structures"; i.e. in all five chains. But they did not consider what this might imply.

Some years later O'Keeffe and I (M. O'Keeffe and B.G. Hyde, 1978), unaware of this, made a similar observation from an analysis of *all* the (then) well-determined structures of silicates and silicas containing corner-connected SiO_4 tetrahedra - framework, sheet and chain structures. Nearest-neighbour distances d(Si...Si) showed a remarkably narrow range, Figure 5; especially if one excluded the small "tail" at high d values, which could be readily justified (M. O'Keeffe, B.G. Hyde, 1978). The average separation was $\langle d(\text{Si...Si})\rangle = 3.06 \pm 0.06$ Å (cf. Bragg and Claringbull's 3.05 Å); a range of only ± 2%. This may be compared with the distribution of Si-O bond lengths in the same structures: $\langle \ell(\text{Si-O})\rangle = 1.64 \pm 0.06$ Å; a range of ± 3.7%. The Si ...Si distance is as constant as the Si-O distance!

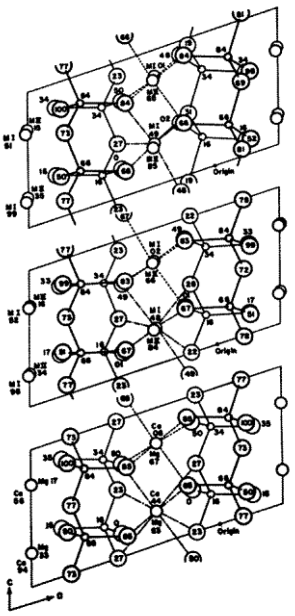


FIGURE 4. Conformations of $(SiO_3)^{2-}$ chains of corner-sharing SiO_4 tetrahedra in various monoclinic pyroxenes, $M^{2+}SiO_3^{2-}$ top - clinoenstatite centre - pigeonite; bottom - diopside. Numbers are atom distances above projection plane in units of *b*/100 (Bragg and Claringbull, 1965). Small circles are Si, medium circles are M, and large cirles are O atoms.

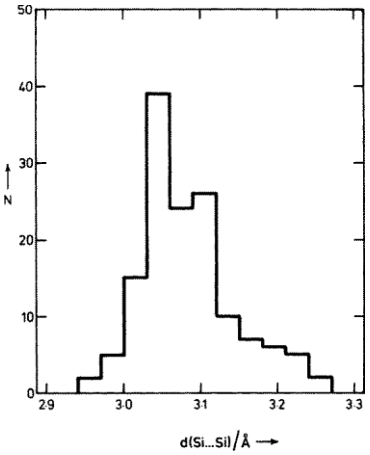
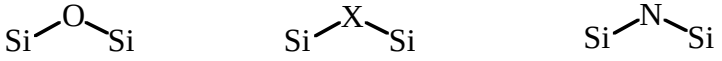


FIGURE 5. Histogram showing the distribution of nearest-neighbour silicon...silicon distances, *d*(Si...Si), in known structures with corner-connected SiO_4 tetrahedra.

Furthermore, *d*(Si... Si) is about the same in small gas molecules containing the same structure element (a) (such as $(H_3Si)_2O$), *viz.* 3.10 ± 0.04 Å; and in silica glasses, *d* = 3.00 to 3.10 Å. It even seems to be independent of the bridging atom, X in structure element (b). For X = NH, $\langle d(Si...Si)\rangle$ = 3.06 ± 0.05 Å in small gas molecules and, in solids with structure element (c) such as α-Si_3N_4 and Si_2N_2O, $\langle d(Si...Si)\rangle$ = 3.01 Å. And, in the gas molecule $(H_3Si)_2CH_2$, *d*(Si...Si) = 3.15 Å. Of course, if the bridging

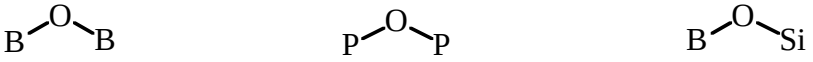


(a) (b) (c)

atom X is different then so is the bond length, ℓ(Si-X), and the bond angle, $\angle$(SiXSi). The approximate values of these parameters (ℓ / $\angle$) are for X = O, N and C respectively, 1.65 Å / 147˚, 1.70 Å / 120˚ and 1.88 Å / 109˚.

All this suggested that, in some sense, the bridged Si atoms were touching: a sort of van der Waals contact;* and that *with only one bridging atom* (the "*one-angle*" case) the silicon radius for such *non-bonded*, Si...Si interactions was R(Si) ! 3.06/2 1.53 Å, Figure 6.

Similar observations were made for borates with bridges (d), phosphates with bridges (e), and so on. Furthermore, such radii were additive; e.g. in borosilicates with B-O-Si bridges (f), $\langle d(\text{B...Si})\rangle$ = 2.80 Å , compared with R(B),R(Si) = 1.26 + 1.53 = 2.79 Å (Tables 1 and 2).



(d) (e) (f)

Such an approach had previously been put forward for small gas molecules both organic and inorganic, especially by Bartell (1968), but not for non-molecular solids. The extension to the latter is consistent with the more recent approaches by quantum methods in which the likely structures of solids are deduced by calculations on small gas molecules with similar structure elements (G.V. Gibbs, 1982; M. O'Keeffe, M.D. Newton and G.V. Gibbs, 1980; J.K. Burdett and D. Caneva, 1985). A crystal is just a molecule with a large (very large!) molecular weight.

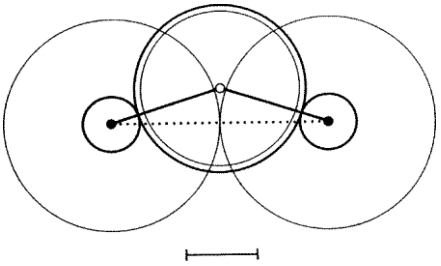


FIGURE 6. Geometry of the SiOSi link (a) between a pair of corner-connected SiO_4 tetrahedra: ℓ (Si-O) = 1.61 Å, d (Si ... Si) = 3.06 Å. Heavier circles are the "crystal radii" of Shannon (1976), lighter circles are non-bonded radii, R, for Si and O. (Small filled circles = Si, small open circle = O. Bar = 1 Å)

TABLE 1

'One-Angle' Radii (in Å) Appropriate to BB' Contact in B-X-B' 'Configurations'

Be	B	C	N	O	F
1.39	1.33	1.25	1.14	1.13	1.08
	Al	Si	P	S	Cl
	1.63	1.55	1.46	1.45	1.44
	Ga	Ge	As	Se	
	1.63	1.58	1.58	1.58	

* Dubbed by Ted Summerville "close encounters of the second kind" (E.W. Summerville, 1977)

The new notion is therefore that non-bonded *interactions* between second (and perhaps more distant) nearest neighbour atoms can be an important factor in determining the geometry (and, as will be suggested, the thermodynamic stability) of a structure; and that *cation...cation interactions may well be the more important*, because the *R* values of cations are usually larger than those of anions, certainly of the first-row anions, N, O and F.

As I indicated earlier, organic chemists have long realised the importance of non-bonded interactions, and developed the science of conformational analysis. Inorganic molecules - even the giant ones that are "non-molecular" crystals - are, in principle, no different.

TABLE 2

Observed Bond Angles in Cristobalites Compared with those Calculated for Non-Bonded Cation-Cation Contact

	Observation	Calculated
Si-O-Si	147°	149°
Ge-O-Ge	128	129
B-O-P	133	138
Be-O-S	136	134
Al-O-P	145	143
B-O-As	128	134
Si-O-Al		143
Al-O-Al		139
Ga-O-P	135	
Be-F-Be	~140*	127

* Estimated from lattice constant.

The hard-sphere model implied by a non-bonded radius should, of course, be replaced by a potential energy curve which shows the interaction energy as a function of (non-bonded) interatomic separation; also a well known concept, Figure 7.

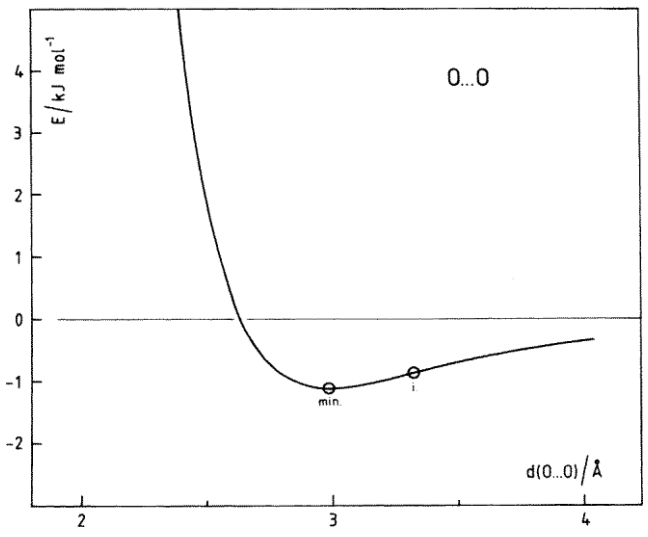


FIGURE 7. Typical potential energy curve characteristic of non-bonded interactions

Thus, qualitatively at least (we do not yet have such potential energy curves for cations), we can understand why for example ⟨-quartz and cristobalite have their observed structural geometries. In both cases (topologically different, but flexible) frameworks of corner-connected SiO_4 tetrahedra are collapsed from their most open possible geometries (which they would be expected to have if they were ionic). The extent of the collapse is just that which reduces *d*(Si...Si) to ~ 3.06 Å. And, furthermore, in SiO_2 one has SiO_4 tetrahedra rather than SiO_6 octahedra, not because one cannot pack more than four oxygens around a silicon (as the ionic model would have it) - one can, cf. $^{VI}Si^{IV}P_2^{II}O_7$ - but because if one does one must then pack more than two silicons around an oxygen: $^{>IV}Si^{>II}O_2$. That means a minimum of three, $^{VI}Si^{III}O_2$. But that is not possible because then *d*(Si...Si) will be significantly less than 3.06 Å, and so extremely repulsive (cf. Figure 7). Compare a maximum ⌊(SiOSi) = 120˚ for C.N.(O) = 3 with the observed ⌊ ≈ 147˚ for C.N.(O) = 2 in quartz etc. (High pressure can overcome such repulsions, and SiO_2 then becomes rutile type, $^{VI}Si^{III}O_2$; but with strong Si...Si repulsion).

Summary

The above has been sketchy and incomplete, but it leads to the following simple (somewhat over-simplified) picture of a crystal structure: nearest neighbour atoms are held together by very strong attractive forces (bonds, which are strong enough to overcome nearest neighbour interatomic repulsions) and these bonds are somewhat stretched by the repulsions between the second-nearest neighbour atoms surrounding a central atom (cations around a central anion, and *vice versa*). Thus, in a structure there is a balance between tensile forces (in the bonds) and compressive forces (in the non-bonded interactions) - a normal state of affairs in all structures, including the Sydney Harbour Bridge. The repulsions arise from the Pauli exclusion principle (due to electron orbital overlap). For non-bonded interactions these will correspond to much lower electron densities than occur across bonds - hence non-bonded distances are larger than bonding distances. They do not correspond to electrostatic repulsions between ions (which have a different form): this we can see by the inability of the electrostatic ionic model to account for the observed geometries of flexible structures, such as quartz and cristobalite (R. Fischer and J. Zemann, 1975), calcium-chloride-type structures [as compared with the topologically identical rutile types (H. Bärnighausen *et al*., 1984)], etc.

The relative importance of the two sets of second-nearest neighbour interactions (cation... cation and anion... anion) depend not only on the relative (non-bonded) sizes of the atom types but also on their relative numbers in the crystal, i.e. on the stoichiometry of the compound. Clearly, a preponderance of cations (e.g. Li_3N) will tend to make cation... cation repulsions the more important *because there are more of them* and therefore their average separation is less (than that of the anions). The converse is likely to be true for a crystal of e.g. AlF_3. But in less extreme cases the interplay of stoichiometry and size is a subtle problem.

We are now ready to consider some consequences of this new way of thinking about structures.

The Bulk Modulus of Diamond

Diamond is one of the "hardest", most incompressible substances known. It is also one of the best thermal conductors (better than Ag and Cu) but, under normal conditions, metastable with respect to graphite. The first two facts are often wrongly attributed to rigidly oriented sp^3 hybrid orbitals, used for C-C bonding. But all follow from the fact that the second-nearest neighbour distance, d(C...C) = 2.52 Å, is very close to $2R$(C) = 2.50 Å; and therefore non-bonded contacts are strongly repulsive (cf. Figure 7).

From the equation for the potential energy of C...C contacts (A.I. Kitaigorodsky, 1973) one calculates E ! 17 kJ per mole of contacts, ! 100 kJ per mole of carbon. (Each C atom has 12 C... C contacts, and so there are 6 moles of C... C contacts per mole of C). This is very high: greater than many enthalpies of transformation between structures (or even chemical reactions). Any deformation or compression of the crystal must cause some shorter distances d(C...C), and therefore a steep increase in the repulsive energy, E. Hence the high bulk modulus (4.4 Mbar), and stiffness (which causes the high thermal conductivity), and instability with respect to graphite (in which the lower C.N., ^{III}C instead of ^{IV}C, reduces the repulsion energy mainly by reducing the number of second-nearest neighbours by a factor of four) are all readily accounted for. A more sophisticated analysis (M. O'Keeffe and B.G. Hyde, 1981) reveals that ~ 80% of the bulk modulus arises from these non-bonded repulsions (and also that our picture of stretched bonds and compressed non-bonded contacts is correct).

High pressure is necessary to overcome these repulsions and synthesise diamond. The same is true for the synthesis of the isostructural BN (with d(B...B) = 2.56 Å, cf. $2R$(B) = 2.52 Å). SiC is similar [d(Si...Si) = 3.07 Å , cf. $2R$(Si) = 3.06 Å]. And these are three of the most incompressible substances known. (In contrast all other isostructural compounds, in which $d >> \sum R$, are relatively soft and compressible, e.g. ZnS.)

High Pressure Phase Transformations

Most high-pressure transformations involve an increase in coordination number, e.g. tetrahedral ZnS types transform to octahedral NaCl types: $^{IV}Zn^{IV}S \xrightarrow{P} {}^{VI}Na^{VI}Cl$. [Italic letters indicate a structure type (as distinct from a compound)]. This is to be interpreted in the following way. In such cases the strongest repulsions are between *first*-nearest neighbours, i.e. bonded atoms (cf. the relatively short distances involved, i.e. bond lengths). And it is these repulsions which are relieved by an increase in coordination number for, paradoxical though it may seem at first sight, it results in an *increase* in bond length: more bonds are formed; they must therefore each be weaker, and therefore longer - and this in spite of the decrease in volume (which Le Chatelier's Principle tells us must occur in a high-pressure transformation). For $ZnS \longrightarrow NaCl$ the change in linear dimensions (unit cell edge, and cation-cation = anion... anion distance) is ~ -2.2%, but the change in bond lengths is ~ +5.6%.

But there are some cases, e.g. *olivine* $\xrightarrow{P}$ *spinel* (of great geophysical interest) and zircon $\xrightarrow{P}$ scheelite, where there is a change of structure without a change of coordination number: both the olivine and the spinel forms of magnesium silicate are $^{VI}Mg_2{}^{IV}Si^{IV}O_4$. In such cases the transformation clearly does *not* relieve first-neighbour repulsions. So (we might suggest) perhaps it relieves second-nearest neighbour repulsions? In the olivine/spinel case there is a volume change of ~ -10%; but the anions in the former are approximately in hexagonal eutaxy and in the latter in cubic

eutaxy and so anion/anion C.N.s. are unchanged: on the average, anion-anion distances are reduced in the transformation (thereby probably increasing their repulsive energies). At the same time, *d*(Mg...Mg) is also reduced (by ~8%), but *d*(Mg...Si) is increased by ~3% (See Table 3). This suggests that the transition relieves strong Mg...Si repulsions (at the cost of stronger Mg...Mg repulsions) which, amongst other facts, is consistent with an increase in the C.N. of Si by Mg from 9 in olivine to 12 in spinel.

TABLE 3

Mean Shortest Non-Bonded Distances (in Å) in the ⟨- and ©-Polymorphs (Olivine and Spinel Forms) of Mg_2SiO_4

	⟨-form	©-form	Difference, Δ(©-⟨)
Mg...Si	3.26_5 (2.69_2-3.28_3)	3.36_6	$+0.10_1$
Mg...Mg	3.11_5 (2.99_3-3.86_2)	2.87_0	-0.24_5
O...O	2.91_2(2.55_8-3.39_3)	2.85_2 (2.70_3 -3.00_0)	-0.06_0

Other explanations of the effect of pressure on the relative stabilities of olivine and spinel polymorphs have previously been offered. That of Kamp (1968) is widely accepted. Although it involves Pauling's rule about the relative instability of shared (anion... anion) polyhedral edges it is also perfectly consistent with the explanation given above, which implies that olivine-type Mg_2SiO_4 is destabilised by Mg...Si repulsions (at high pressure) and its spinel-type by Mg...Mg repulsions (at low pressure).

Cation Arrays in Crystal Structures

That cation...cation repulsion is often more important than anion...anion repulsion is consistent with the regularity often observed in the cation arrays of many structures, especially those in which no regularity (simple geometrical pattern) can be detected in their anion arrays. This leads to simple descriptions of many (chemically simple) compounds, such as sulphates, carbonates and silicates of large (especially Group I or Group II) cations, for which no simple geometrical description was previously available (R.W.G. Wyckoff, 1968). We give only a few examples of the many that are possible (M. O'Keeffe and B.G. Hyde, 1985).

1. La_2O_3

The A-type rare earth sesquioxide structure, of which La_2O_3 is the prototype, is far from straightforward in terms of its anion array. This consists of eutactic layers of anions normal to its hexagonal *c* axis, but the interlayer spacings are far from eutactic. The cations are 7-coordinate, in the form of a mono-capped octahedron. On the other hand the cations also form eutactic layers normal to *c*, and their layer spacing is very close to that in ideal hexagonal eutaxy. The structure is therefore most simply described as hexagonally eutactic La, with alternate interlayers occupied by O in all the octahedral sites or O in all the tetrahedral sites, Figure 8. This is rather satisfying, as the former layer is *NaCl* type (to be expected for LnX compounds of the lanthanides, e.g. LaN) and the latter is *CaF_2* type (to be

expected for LnX_2 compounds of the lanthanides, e.g. LaOF). It is therefore not surprising that La_2O_3 (of intermediate stoichiometry) is a simple intergrowth of alternating layers of the two extreme stoichiometries.

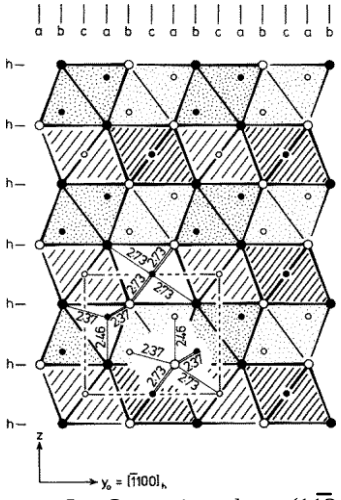


FIGURE 8. The structure of A-type La_2O_3 projected on $(1\bar{1}20)$ of its hexagonal unit cell, and emphasising O-centre La_6 octahedra and La_4 tetrahedra. The cations (larger circles at heights O (open) and 1/2 (filled) are *hcp*. *a*, *b*, c indicate stacking positions of eutactic layers in the usual way; *h* indicates *h*exagonal eutaxy.

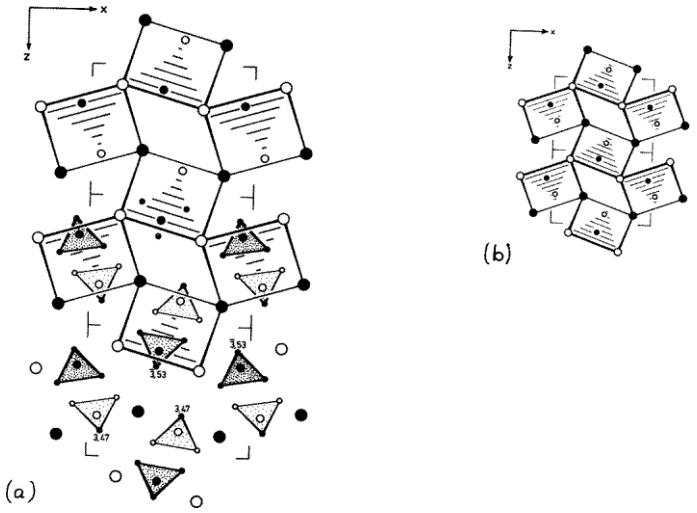


FIGURE 9. (a) The structure of $BaSO_4$ as SO_4 tetrahedra and Ba atoms (below) and SBa_6 trigonal prisms (above).
(b) The structure of FeB: compare with BaS in (a)

2. $BaSO_4$

This is less obvious than the previous example, and a puzzle (R.W.G. Wyckoff, 1968) until now. The anion array is quite irregular; only SO_4 tetrahedra can be recognised. But the BaS array is a simple alloy structure, the *FeB* type, cf. Figure 9.

3. ®-K_2SO_4

This is a structure type of considerable interest in a number of ways (some of which we shall see later) , and is the structure of many compounds. But, as with $BaSO_4$, the only apparent regularity in the structure is in the cation array. The K_2S part is the well-known *Ni_2Si / $PbCl_2$* structure type, Figure 10.

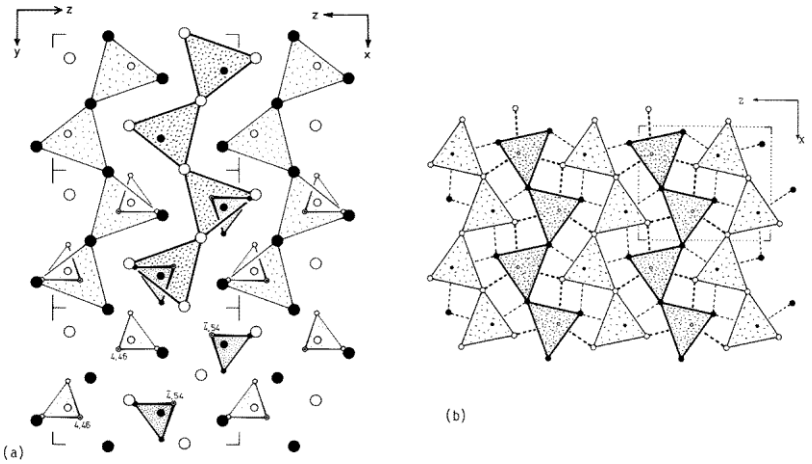


FIGURE 10. (a) The structure of ®-K_2SO_4 shown as SO_4 tetrahedra and K atoms (below) and SK_6 trigonal prisms above. (The unit cell settings are *Pnma* for the axes at top right, and *Pmnb* for those at top left.)

(b) The $PbCl_2$ structure: compare with K_2S in (a)

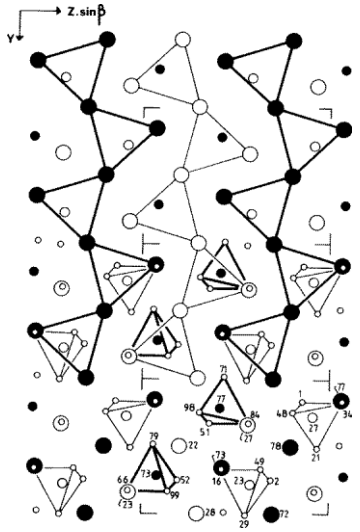


FIGURE 11. The structure of ®-Ca_2SiO_4: compare FIGURE 10

4. Ca_2SiO_4

This substance is polymorphic being able, at different temperatures, to occur in five different structures: ⟨, ⟨'∩, ⟨'L, ® and ©. It is an important component of cement, to the production of which the ©/® polymorphism (close to room temperature) is important. The ®-form, shown in Figure 11, is rather close to the
®-K_2SO_4 type (above), the difference being mainly a very slight deformation of the unit cell and tilt of the BX_4 tetrahedra (SiO_4 and SO_4 respectively). The structure ⟨'L is even closer to ®-*K_2SO_4* ; and the ⟨'H structure *is* ®-*K_2SO_4*. In all three (®, ⟨'L and ⟨'H), the only regularity is in the cation array which is, at worst, a very slightly deformed *Ni_2Si / $PbCl_2$* type.

This case is particularly interesting as the structure of the compound Ca_2Si is also *Ni_2Si* type; i.e. the Ca_2Si arrays in Ca_2Si and in ®'-, ⟨'L-, and ⟨'H-Ca_2SiO_4 are

virtually identical. Furthermore, their molar volumes are also almost the same, 49.9 and 51.8 cm^3 mol^{-1} for Ca_2Si and ®-Ca_2SiO_4 respectively.

These two facts seem at first sight surprising. The first at least appears to be another consequence of cation...cation repulsion, as does the complex modulated structure of ⟨'$_L$-Ca_2SiO_4 [by analogy with the experimental results for ⟨'$_L$-Sr_2SiO_4 (Hyde, Sellar and Stenberg, 1986)]. But this is too specialised a problem to be dealt with here. Instead, we turn to some elementary chemistry.

The Chemistry of Some Simple Binary Fluorides, Oxides etc.

(M. O'Keeffe and B.G. Hyde, 1984)

Consider the "normal" oxides of the alkali metals, Li to Cs; i.e. those in which the metal and the oxygen have their normal valences (of 1 and 2 respectively) and in which there are only metal-oxygen bonds (which means we exclude peroxides etc. with O-O bonds and suboxides with metal-metal bonds). Their stoichiometry is M_2O: twice as many cations as anions; and "large" cations too, so that cation...cation repulsions are likely to be important - as turns out to be the case.

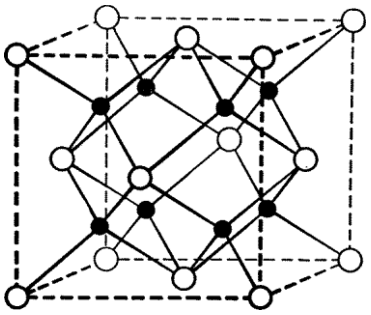


FIGURE 12. The fluorite-type structure: smaller circles are anions, larger ones are cations.

All except Cs_2O have the antifluorite structure (Figure 12), in which each oxygen is 8-coordinate and each metal is 4-coordinate, $^{IV}M_2{}^{VIII}O$.* A striking fact is that these oxides are quite difficult to prepare: instead of the normal oxides one readily gets peroxides M_2O_2 (with $O\text{-}O^{2-}$) and/or superoxides MO_2 (with $O\text{-}O^{-}$). And, if prepared, they are extremely reactive - with CO_2 and H_2O in the atmosphere, etc. Put formally, their reactions are extremely exothermic, due to their enthalpies of formation being low. Less formally, they are relatively unstable, and this shows clearly from their low bond enthalpies (M. O'Keeffe and B.G. Hyde, 1984), (Figure 13), and correspondingly long bond lengths (N.K. McGuire and M. O'Keeffe, 1984). For the same formal bond valence** the bond enthalpies are larger (and the bonds correspondingly shorter) in ternary compounds with lower stoichiometric ratios cations/anions, and also in peroxides etc.

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* Note in passing the high C.N. for the small O and low C.N. for the large M; and compare the radius ratio rules.

** Bond valence (or bond strength) is, for equivalent bonds (as in fluorite types), simply the formal valence of an atom divided by its C.N. In the case of e.g. $^{IV}K_2{}^{VIII}O$ it is 1/4 at K = 2/8 at O. This shows how coordination numbers and stoichiometry are unavoidably related.

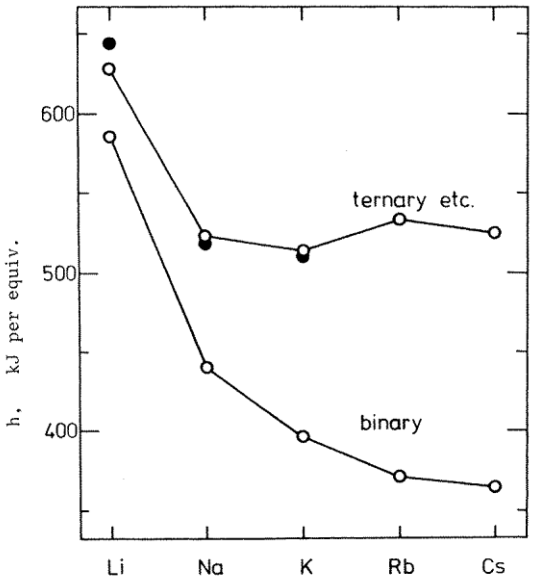

FIGURE 13. Equivalent bond enthalpies (h) of alkali metal-oxygen bonds in binary (M_2O and ternary oxides. (The filled circles are for peroxides, e.g. Na_2O_2: note that their h values correspond to those for the ternary compounds, i.e. the Na-O bonds are stronger in Na_2O_2 than in Na_2O.)

This decreased stability we attribute to excessive cation...cation repulsion in the normal binary compound. One can imagine the M_2O compound being formed by shrinking an infinitely spaced, anti-fluorite-like array of cations and anions. As the eight cations approach the anion to which they are coordinated (Figure 14) the bond lengths decrease (and bond enthalpies increase) as do the non-bonded distances and repulsions. Before the cations attain a distance from the anion appropriate to a bond valence of 1/4, the attractive (bonding) forces are balanced by the repulsive (M...M) non-bonded interactions, and the bonds remain stretched and weak. The deficit in bond enthalpy is ~ 60 kJ mol^{-1} in Li_2O increasing to ~ 330 kJ mol^{-1} in Rb_2O (Figure 13). Hence the high ΔH^0 values for reactions of these oxides which involve a decrease in anion C.N.

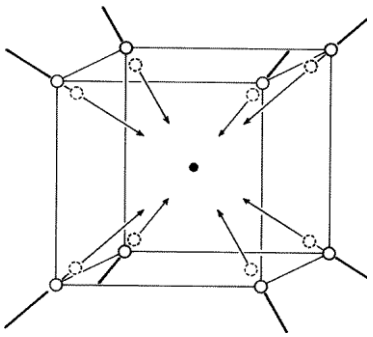

FIGURE 14. Notional formation of OM_8 group in antifluorite-type (normal) alkali metal oxides, M_2O, by contracting an infinitely separated atom array. Filled circle = O; open circles = M, continuous at actual positions, broken at ideal positions (bond valence = 1/4).

Using accepted bond valence/bond length relations (those of I.D. Brown *et al.*, 1985, but see also N.K. McGuire and M. O'Keeffe, 1984) one can deduce expected bond lengths

in M_2O, and compare them with the observed values (Table 4). As with the bond enthalpies, the discrepancy increases with increasing atomic number of the cation.

TABLE 4

Expected and Observed ℓ(M-O) in *Antifluorite-Type Alkali Metal Oxides,* M_2O

M =	Li	Na	K	Rb
Expected ℓ/Å	1.9_3	2.2_4	2.4_3	2.5_4
Observed ℓ/Å	2.00	2.40	2.79	2.93
Difference $\Delta\ell$/ Å	0.0_7	0.1_6	0.3_6	0.3_9
Difference /%	3.5	7.2	14.8	15.0

A similar, though less drastic, effect is observed in the oxides of the Group II (alkaline earth) metals. This mitigation is a result of the lower stoichiometric ratio cations/anions in the latter; due to the cation valence being higher than for Group I. Similarly, the stoichiometric ratio is reduced for Group I cations if the anion valence is reduced, i.e. for fluorides instead of oxides; and the bond enthalpy deficit is correspondingly smaller (M. O'Keeffe and B.G. Hyde, 1984).

Conversely, increasing the valence of the anion should increase the severity of the problem. (There will now be even more cations per anion.) So consider the nitrides of Group I, M_3N: for the heavier M atoms the bonds are so weakened that the compounds do not form: only Li_3N is known. (Instead one gets azides, $M(N_3)$, with the polyanion N_3^- cf. the reference to peroxides etc. above.) And for carbides, M_4C, the situation is of course worse: none is known. For Group II metals only one "normal" carbide is known, Be_2C. And even for Group III one has only boron carbides and Al_4C_3. (Instead one tends to get polyanions, e.g. "acetylide" C_2^{2-}, or metal-metal bonding, i.e. polycations, e.g. Ca_2N, $Ca_{11}N_8$ etc.)

Thus, a lot of simple chemistry falls into place. And there is much more (M. O'Keeffe and B.G. Hyde, 1984), all of which appears to be a natural consequence of *"cation crowding"*, which gets worse as the stoichiometric ratio (cations/ anions) gets higher.

I submit that what has been said is more than enough to indicate that cation size is a significant factor in solid state physics and chemistry and mineralogy; and that this notion is worth pursuing in the future.

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