JOURNAL OF SOLID STATE CHEMISTRY 39, 265–267 (1981)

Cation Packing and Molar Volume in Oxides and Nitrides with the Wurtzite Structure

In the traditional view of crystals such as oxides, nitrides, etc., the basic structural principle is supposed to be that they are made up of a close-packed array of large anions "in contact" with small cations in the interstices of the array. There is in fact neither an experimental nor a theoretical basis for this supposition (*1*). We have shown that in contrast, at least for compounds with first-row anions, cation–cation nonbonded interactions are far more important than anion–anion interactions.

In a recent review (*2*) we have discussed the nature of the nonbonded interaction potential. In oxides etc. it is a very strong function of cation–cation distance at nearest-neighbor separations, and at further distances relatively unimportant. Thus in some instances, such as those involving *flexible* framework structures (e.g., polymorphs of SiO_2 like cristobalite and quartz), the potential can be replaced by that for a hard sphere of radius R. We first introduced such nonbonded radii into crystal chemistry in a discussion of compounds with structures topologically equivalent to that of cristobalite (*3*). In that work we showed that in compounds ABO_4, A–O–B bond angles could be accurately predicted using A–O and B–O bond lengths and the nonbonded radii of A and B (the latter taken from data on molecular configurations).

We subsequently discussed the relative stability of tetrahedral structures (wurtzite, zinc blende, etc. (*4*)). We pointed out that in compounds that had only a wurtzite (but not a zinc blende) polymorph, the cation–cation distance was close to the sum of the nonbonded radii and concluded that existence of only a wurtzite polymorph was due to this fact. In such compounds we further deduced that nonbonded cation–cation repulsions were responsible for the axial ratios being less than the value $(8/3)^{1/2} = 1.633$) for ideal hexagonal closest packing. In the same paper we discussed compounds $ABXY$, where X, Y = O or N, isostructural with β-$NaFeO_2$. These are orthorhombic superstructures of the wurtzite structure—for all these, the psuedo-hexagonal cell parameters have $c/a < (8/3)^{1/2}$ (ranging from 1.565 to 1.631). Two further points concerning these quaternary or ternary compounds are relevant.

1. The anion packing is typically halfway between that of hexagonal close packing and that of the "ideal high cristobalite" structure of one-half the density (*3*).

2. In general, the volume per unit cell of the oxides is greater than that of the nitrides, although it is generally conceded that the radius of the nitride ion is greater than that of the oxide ion (but see O'Keeffe (*5*) for a discussion of nitride ion radii based on an ionic model).

In this paper we examine the extent to which the volume of these crystals is determined by cation nonbonded radii. We use nonbonded radii given earlier (*6*). Data for seven β-$NaFeO_2$ structure compounds containing elements for which nonbonded radii are available have been listed before (*4*). There are also known LiSiON (with a = 5.19 Å, b = 6.39 Å, c = 4.742 Å quoted by Jack (*7*)), ZnAlON (*8*) (a = 5.332 Å, b = 7.006 Å, c = 5.109 Å) and MgAlON (*8*) (a

0022-4596/81/110265-03$02.00/0

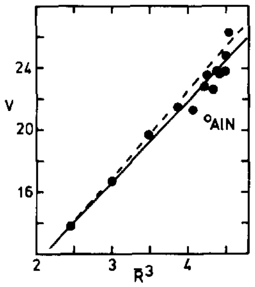

FIG. 1. The volume per cation (V) plotted against the cube of the mean nonbonded radius ($\bar{R}^3$). The full line is the linear regression excluding the datum for AlN. The broken line gives the volume for closest packing of spheres of radius $\bar{R}$.

= 5.361 Å, b = 6.937 Å, c = 5.079 Å). There are also four binary wurtzites (ZnO, BeO, AlN and GaN) for which nonbonded radii are available.

For these compounds we have plotted V, the volume of the crystal per cation (or per anion) against $\bar{R}^3$, where $\bar{R}$ is the mean cation nonbonded radius, in Fig. 1. With the exception of the point for AlN (omitted in the numerical analysis) the points fit closely about a straight line. A least-squares fit of an expression,

$$V = a\bar{R}^3 + b, \qquad (1)$$

gave $a = 5.19$, $b = 1.14$ Å^3. The correlation coefficient $r = 0.979$, showing that the volume is almost perfectly predicted by the cation nonbonded radii. It might be noted that correlations such as $V^{1/3}$ with cation *ionic* radii are significantly worse ($r = 0.88$). And clearly the volumes are not related in any meaningful way to *anion* radii.

Also shown in Fig. 1 (dashed line) is the volume for ideal close packing of spheres of radius $\bar{R}$. The data fall close to this line. However, the volumes are slightly smaller supporting our contention that in wurtzites with $c/a < (8/3)^{1/2}$, the cations are somewhat compressed.

It is not entirely clear why AlN is anomalous. Equation (1) predicts $V = 23.2$ Å^3 and the observed value is $V = 20.7$ Å^3—a large discrepancy. We (*4*, *6*) have speculated that when cation—cation repulsions become too large, structures derived from that of β-BeO become more stable. It is interesting that AlN also has another form (δ-AlN) which is quoted to be hexagonal (*9*) but which could in fact have the strongly pseudo-hexagonal β-BeO structure.

In conclusion it should be emphasized that the correlation of Fig. 1, which is really very good, relates the volumes of *crystals* to cation nonbonded radii which originally came from a consideration of the geometries of *molecules*. This suggests that an atomic, rather than ionic, description of these crystals is the more appropriate. From this point of view it is not surprising that atoms such as Al and Si should be much "bigger" than atoms such as N and O.

Acknowledgment

This work was supported by Grant DMR 78-09197 from the National Science Foundation.

References

1. M. O'KEEFFE, *Acta Crystallogr. Sect. A* **33**, 924 (1977).
2. M. O'KEEFFE AND B. G. HYDE, *in* "Structure and Bonding in Crystals" (M. O'Keeffe and A. Navrotsky, Eds.). Academic Press, New York (1981).
3. M. O'KEEFFE AND B. G. HYDE, *Acta Crystallogr. Sect. B* **32**, 2923 (1976).
4. M. O'KEEFFE AND B. G. HYDE, *Acta Crystallogr. Sec. B* **34**, 3519 (1978).
5. M. O'KEEFFE, *Acta Crystallogr. Sect. A* **35**, 776 (1979).
6. M. O'KEEFFE AND B. G. HYDE, *Trans. Amer. Crystallogr. Assoc.* **15**, 65 (1979).
7. K. H. JACK, *J. Mater. Sci.* **11**, 1135 (1976).
8. C. L. SHAVERS, Ph.D. dissertation, Arizona State University (1981).

9. Y. Uemura and M. Iwata, *J. Mater. Sci.* **13**, 208 (1978).

M. O'Keeffe and C. L. Shavers
Department of Chemistry
Arizona State University
Tempe, Arizona 85281

B. G. Hyde
Research School of Chemistry
The Australian National University
Canberra ACT 2600, Australia

Received April 30, 1981