

Volume Chemistry of Nitrogen in Binary Metal Nitrides and Subnitrides

Welf Bronger*, Rüdiger Kniep and Miroslav Kohout

Introduction

In 1934, W. Biltz published his book "Raumchemie der festen Stoffe" ("Volume Chemistry of Solids") [1] attempting to approximate the volume demand of solids by a sum of individual atom or ion increments. For determining volume increments, statistical averages based on the data available at that time were used. The averages were utilized to set up tables for volume increments. Complementarily, deviations were being discussed in dependence on the type of bonding and of the partners involved in the compound, thus producing justification for the alternatively suggested title of the book "Die Bindungsart der Atome, raumchemisch beurteilt" ("The Bonding Type of Atoms, Assessed from the View of Volume Chemistry"). That concept has not decisively won recognition over the one based on the additivity of radii of spherical-shaped particles, mainly propagated by V. M. Goldschmidt. The following will show that a combination of the model developed by Biltz with modern quantum mechanical calculations of atomic volumes enables insights into bonding relationships which are inaccessible via the discussion of interatomic distances.

The determination of partial volumes of atoms or ions on a quantum mechanical basis are founded, for the most part, by the works of R.F.W. Bader [2,3]. According to the latter, a subsystem, such as an atom in a crystalline compound, is bounded by the surface of zero-flux of the electron density gradient vector field. Furthermore, the parallelism existing between the form and the properties leads to the determination of the charge distribution among the atoms.

The analysis of the electron localization function (ELF) permits further insight into the bonding situation in real space. The function was introduced by A. D. Becke and K. E. Edgecombe as a relative measure for the probability of finding an electron in the vicinity of another same-spin electron [4]. In the time following, alternatives to the original mathematical formulation became known [5,6]; chemists soon adopted this method for the purpose of interpreting relationships within bonds in familiar terms.

Since the publication of the volume increments by W. Biltz, the amount of data material serving as the basis for calculation mean values has considerably grown, owing mainly to the results of crystal structure determinations available. This process revealed that volume-chemical problems can only reasonably be treated within individual groups of compounds since, according to the concept of volume increments, there exist systematic dependences on the structure and on the type of bonding, in analogy to the ionic and atomic radii. Dependences on the type of bonding are of particular impact if strongly polarizable anionic partners are discussed. For instance, the volume increment of hydrogen in metal hydrides ranges from 13.7 cm³/mol in cesium hydride to 3.9 cm³/mol in palladium hydride [7]. An analogous dependence can be expected for metal nitrides.

Biltz's volume increments and partial volumes according to Bader

Table 1 juxtaposes the volumes $V_B^c(N)$ [8] of nitrogen according to Biltz with the volumes $V_\rho(N)$ determined by Bader's method (ρ basins); for the latter, the individually determined charge excess is stated relative to the neutral nitrogen atom in units of the electron. Biltz's volume increments for the cations (see Table 2) were used to determine the volume $V_B^c(N)$ of the nitride species. For oxidation numbers not included in the table interpolation is applied, e.g., for Ba₃N, the values for Ba²⁺ (16 cm³/mol) and Ba metal (38.2 cm³/mol) lead to the value of 11.1 cm³/mol per electron, whereby one is independent of the formulation Ba⁺ (27.1 cm³/mol) or Ba²⁺ (16 cm³/mol) + e⁻ (11.1 cm³/mol).

In Figure 1, the volumes $V_B^c(N)$ of nitride ions in binary metal nitrides are plotted against the volumes $V_\rho(N)$ (cf. Table 1). It results in a surprising, almost linear relation between both sequences. The findings that the linear least-squares fit shows an almost 1:1 inclination, but has a non-zero positive abscissa value, is due to the fact that the Biltz model is based on ions, i.e., for nitrogen in all cases

	$V_{\rho}(N)$	Excess charge	$V_B^c(N)$
Li_3N	20.3	2.6	22.4
Ca_3N_2	14.0	1.7	18.2
Mg_3N_2	12.8	2.3	15.6
AlN	10.1	2.4	12.1
LaN	9.6	1.7	13.4
ScN	7.9	1.6	11.2
GaN	7.5	1.5	11.4
InN	7.5	1.3	11.8
CrN	5.8	1.4	9.7 ^a
Mn_4N	4.8	1.2	8.9
Fe_4N	4.5	1.1	9.0

^aThe binary nitrides TiN , ZrN , HfN , VN , NbN and TaN give corresponding values.

Tab. 1: Volumes $V_{\rho}(N)$ (in cm^3/mol) of nitride ions, determined as ρ -basins with excess charge (in e^-) as well as volumes $V_B^c(N)$.

the nitride ion N^{3-} is assumed. Nevertheless, the decreasing ionicity, ranging from $\alpha\text{-Li}_3\text{N}$ to the nitrides of iron and manganese, is represented in both sequences quite analogously. Figures 2 and 3 depict, as examples, the ρ -basins of the nitrides Li_3N and CrN .

Special relationships result for metal nitrides classified as metastable compounds, such as Cu_3N [9] and Na_3N [10]. For both nitrides an atomic arrangement corresponding to the ReO_3 structure type was determined. The distances between the cation and the anion are within the expected range [11], in contrast to the much too large volumes $V_B^c(N)$ for the nitrogen anions in relation to $V_{\rho}(N)$ (cf. Table 3 and Fig. 1). If, contrary to that, an

Atom/Ion	Vol. Increm.	Atom/Ion	Vol. Increm.
Al^{3+}	0.5	La^{3+}	9
Ba^{2+}	16	Li^+	1.5
Ba	38.2	In^{3+}	6.5
Ca^{2+}	6.8	Mg^{2+}	2
Ca	26.1	Mn^{2+}	5
Cr^{3+}	1	Mn	7.4
Cu^+	5	Na^+	6.5
Cu	7.1	Na	23.8
Fe^{2+}	4	Sc^{3+}	2
Fe	7.1	Sr^{2+}	11
Ga^{3+}	2	Sr	33.9

Tab. 2: Volume increments (in cm^3/mol) used. The ion increments correlate with the Biltz values [1]. The values for the atoms have been calculated from the element structures.

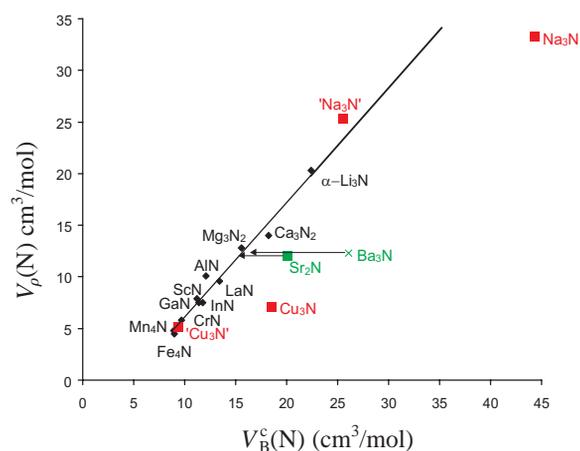


Fig. 1: Volumes $V_B^c(N)$ of nitride ions in selected binary metal nitrides (black) and subnitrides (green) according to Biltz, outlined against the volumes $V_{\rho}(N)$ calculated according to Bader. Red: metastable nitrides and “hypothetic modifications”

atomic arrangement based on the atomic distances is assumed to be in accordance with the $\alpha\text{-Li}_3\text{N}$ structural type (acc. to [12] discussed as one of the possible arrangements for Na_3N), the volumes $V_{\rho}(N)$ and $V_B^c(N)$ arrange themselves within the limits of error into the linear relationship between the two sequences. This applies to Cu_3N correspondingly (see Table 3 and Fig. 1). At this point, it becomes clear once again what complementary information can be provided by volume chemistry of the atoms as opposed to a discussion on atomic distances.

Likewise, the analysis of the atomic volumes permits valuable insight into the bonding situation of the subnitrides of the alkaline-earth metals Ba_3N ,

Lattice parameters in \AA	$V_{\rho}(N)$	Excess charge	$V_B^c(N)$
$\text{Na}_3\text{N}^{\text{a}}$ $a = 4.7317(4)$	33.3	2.1	44.3
$\text{Na}_3\text{N}^{\text{b}}$ $a = 4.23$ $c = 4.82$	25.4	2.1	25.5
$\text{Cu}_3\text{N}^{\text{a}}$ $a = 3.819(1)$	7.2	1.4	18.5
$\text{Cu}_3\text{N}^{\text{b}}$ $a = 3.48$ $c = 3.84$	5.2	1.4	9.3

^a Applies to the experimentally determined structure (ReO_3 -Typ)

^b Applies to the calculated atomic arrangement in the $\alpha\text{-Li}_3\text{N}$ type (cf. text)

Tab. 3: Volumes $V_{\rho}(N)$ (in cm^3/mol) of nitride ions, determined as ρ -basins with excess charge (in e^-) as well as volumes $V_B^c(N)$ for Na_3N and Cu_3N in the experimentally determined modification (ReO_3) and in the hypothetical modification of the $\alpha\text{-Li}_3\text{N}$ type.

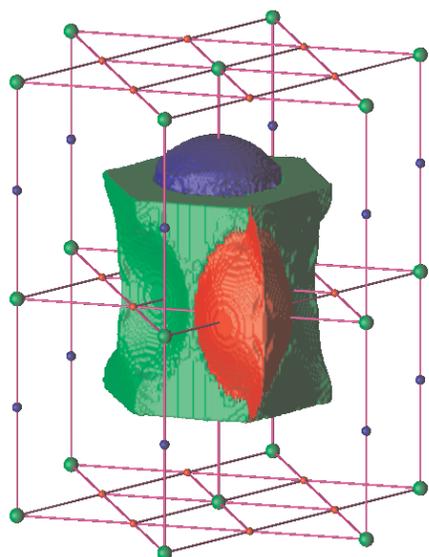


Fig. 2: ρ -basins for α - Li_3N . Red and blue: Li in two crystallographic sites; green: N. The radii of the atomic spheres are proportional to nuclear charges.

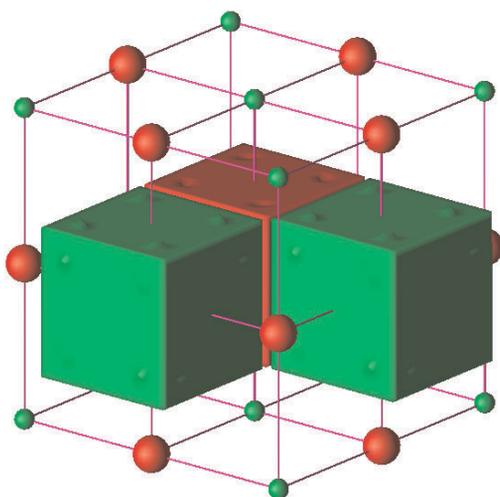


Fig. 3: ρ -basins for CrN. Red: Cr; green: N. The radii of the atomic spheres are proportional to nuclear charges.

Ba_2N , Sr_2N , and Ca_2N , respectively. The atomic arrangement within the subnitride Ba_3N is characterized by one-dimensional stacks of face-sharing barium octahedra, which are centered by nitrogen [13]. Obvious are the large barium-barium distances between the one-dimensional structural units which clearly exceed the distances in barium metal. From theoretical investigations, one possible explanation for this peculiarity is based on the find-

ing that a metallic bonding system exists between the Ba_3N structural units. The electrons participating in this system demand an additional volume [12]. Via the nitrogen volume $V_{\text{B}}^{\text{c}}(\text{N}) = 26.1 \text{ cm}^3/\text{mol}$ in Ba_3N , an analogous interrelation may be recognized. The linear relationship between $V_{\rho}(\text{N})$ and $V_{\text{B}}^{\text{c}}(\text{N})$ relates a Biltz volume of $V_{\text{B}}^{\text{c}}(\text{N}) = 15.4 \text{ cm}^3/\text{mol}$ to the ρ -basin volume of $V_{\rho}(\text{N}) = 12.3 \text{ cm}^3/\text{mol}$ for nitrogen in Ba_3N (cf. Fig. 1). Then, for each Ba^+ results a volume of $30.7 \text{ cm}^3/\text{mol}$ (the total volume of Ba_3N amounts to $107.4 \text{ cm}^3/\text{mol}$). Considering the volume increment of Ba^{2+} ($16 \text{ cm}^3/\text{mol}$), there is a volume of $14.7 \text{ cm}^3/\text{mol}$ per electron, i.e. clearly more than $11.1 \text{ cm}^3/\text{mol}$, a value which results from the difference between Ba metal and Ba^{2+} . This independently confirms the explication given by the authors in [13].

	$V_{\rho}(\text{N})$	Excess charge	$V_{\text{B}}^{\text{c}}(\text{N})$
Ba_2N	12.1	2.1	20.3
Sr_2N	12.1	2.3	20.0
Ca_2N	12.9	2.3	20.5
Ba_3N	12.3	2.1	26.1

Tab. 4: Volumes $V_{\rho}(\text{N})$ of nitride (in cm^3/mol) ions in alkaline-earth metal subnitrides, determined as ρ -basins with excess charge (in e^-) as well as volumes $V_{\text{B}}^{\text{c}}(\text{N})$.

Ba_2N , Sr_2N and Ca_2N crystallize in the CdCl_2 structure type. Here, too, the metal-metal distances between the octahedral layers centered by nitrogen are clearly larger than in the respective metals. The Biltz volumes $V_{\text{B}}^{\text{c}}(\text{N})$, which are too large for the nitride ions (cf. Table 4 and Fig. 1), may similarly be explained by the fact that they were allocated part of the electron volume. If, for example, the nitrogen volume of $15.2 \text{ cm}^3/\text{mol}$ (acc. to the linear relationship, Fig. 1), corresponding to $V_{\rho}(\text{N}) = 12.1 \text{ cm}^3/\text{mol}$ (Fig. 4) for Sr_2N , is applied a value of $16.3 \text{ cm}^3/\text{mol}$ per electron will result. According to the difference in volume between Sr^{2+} and Sr metal, a mere value of $11.5 \text{ cm}^3/\text{mol}$ may be expected. Figure 5 shows an ELF diagram of Sr_2N which reveals the region of higher electron localizability between neighboring Sr_2N layers.

The example calculations performed for crystal structures of binary metal nitrides and subnitrides according to Biltz and ρ -basins according to Bader permit, in mutual comparison, consistent insights into the bonding relationships of these compounds.

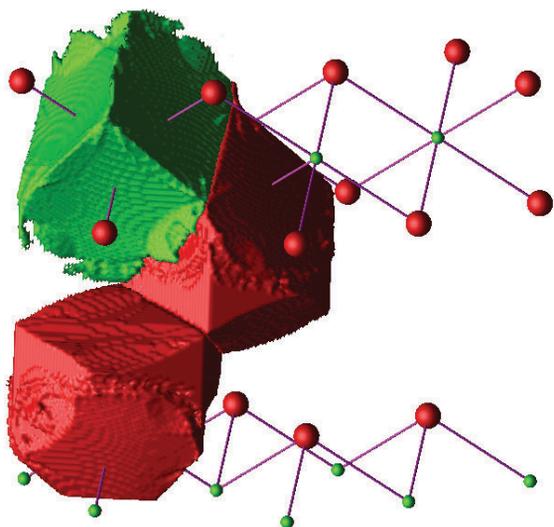


Fig. 4: ρ -Basins for Sr_2N . Red: Sr; green: N. The radii of the atomic spheres are proportional to nuclear charges. The irregular edges and faces of the ρ -basins are artefacts of the basin search program [14].

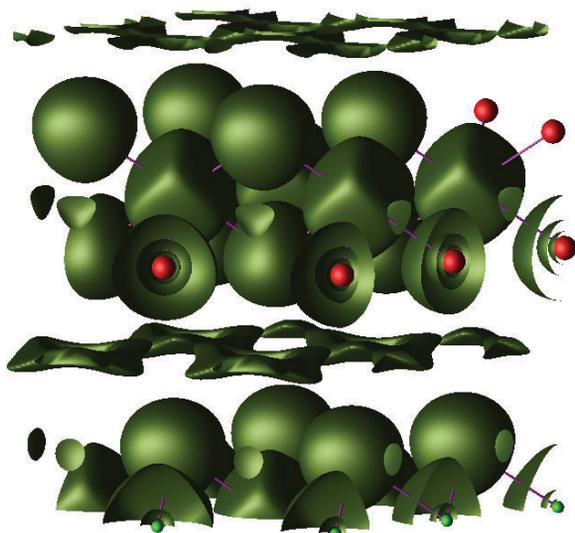


Fig. 5: ELF isosurface for Sr_2N . The green color represents the iso-value of $\eta = 0.5$.

At the same time, it becomes clear that the Biltz volume increments show a quantum-chemical relevance in the chemistry of solids. Finally, the investigation reveals the considerable range of volume demand of a strongly polarizable bonding partner, such as the nitride ion.

References

- [1] W. Biltz, "Raumchemie der festen Stoffe", Verlag von Leopold Voss, Leipzig, 1934.
- [2] R. F. W. Bader, "Atoms in Molecules – A Quantum Theory", Clarendon Press, Oxford, 1995.
- [3] R. F. W. Bader, P. L. A. Popelier and T. A. Keith, *Angew. Chem. Int. Ed.* **33**, 620 (1994).
- [4] A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **92**, 5397 (1990).
- [5] A. Savin, O. Jepsen, J. Flad, O. K. Anderson, H. Preuss, H. G. von Schnering, *Angew. Chem. Int. Ed.* **31**, 187 (1992).
- [6] M. Kohout, *Int. J. Quantum Chem.*, eingereicht.
- [7] W. Bronger, *Z. Anorg. Allg. Chem.* **622**, 9 (1996).
- [8] The indices c and B in $V_B^c(\text{N})$ mean that the nitrogen volumes are determined with respect to the mean cationic increments of Biltz.
- [9] U. Zachwieja, H. Jacobs, *J. Less-Common Met.* **161**, 175 (1990).
- [10] D. Fischer, M. Jansen, *Angew. Chem. Int. Ed.* **41**, 1755 (2002).
- [11] R. D. Shannon, *Acta Cryst.* **A32**, 751-767 (1976).
- [12] M. Jansen, *Angew. Chem. Int. Ed.* **41**, 3746 (2002).
- [13] U. Steinbrenner, A. Simon, *Z. Anorg. Allg. Chem.* **624**, 228 (1998).
- [14] M. Kohout, Program Basin, Version 2.4, MPI CPfS, Dresden (2002).

* Institut für Anorganische Chemie, RWTH Aachen