Pressure-induced suppression of structural distortions manifested in group–subgroup relationships

K. F. Dziubek[1], M. Ceppatelli[2,3], M. Serrano-Ruiz[3], M. Morana[4], D. Scelta[2,3], G. Garbarino[5], T. Poręba[5], V. Svitlyk[5], M. Mezouar[5], A. Sukserm[6], T. Bovornratanaraks[6], U. Pinsook[6], S. Scandolo[7], R. Bini[2,3,8], M. Peruzzini[3]

[1]Institut für Mineralogie und Kristallographie, Universität Wien, Wien, Austria, [2]LENS, European Laboratory for Non-linear Spectroscopy, Sesto Fiorentino, Italy, [3]ICCOM-CNR, Institute of Chemistry of OrganoMetallic Compounds, National Research Council of Italy, Sesto Fiorentino, Italy, [4]Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Firenze, Italy, [5]ESRF, European Synchrotron Radiation Facility, Grenoble, France, [6]Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok, Thailand, [7]ICTP, Abdus Salam International Centre for Theoretical Physics, Trieste, Italy, [8]Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Sesto Fiorentino, Italy

kamil.dziubek@univie.ac.at

Based on widely accepted rules of thumb [1, 2] of high-pressure crystal chemistry, elements at elevated pressure increase their coordination number and behave like the elements below them in the periodic table at lower pressures. It was noted already in the highly acclaimed structural chemistry book by Alexander Frank Wells [3] that the crystal structures of gray arsenic (Strukturbericht A7, space group $R\bar{3}m$) and black phosphorus (bP, Strukturbericht A17, space group *Cmce*) may be regarded as the distorted simple cubic (*sc*, space group $Pm\bar{3}m$) structure (Fig. 1). The ideal *sc* structure is very rare in nature, and relatively unstable because of its low packing efficiency and low coordination number. Further high-pressure studies demonstrated that bP transforms first to the A7 phase and then, passing through a pseudo-simple-cubic structure, to the *sc* phase [4, 5]. A similar pressure-induced phase transition from the A7 to the sc phase is observed in elemental arsenic. Recent reports show that polymeric cg-N (space group $I2_13$) and bp-N (*Cmce*, bP-type structure) phases of nitrogen can also be regarded as distorted *sc* atomic arrangements [6]. Furthermore, recently discovered crystalline arsenic nitride AsN (space group $P2_13$) [7] can be considered as a highly distorted rock salt (Strukturbericht B1, space group $Fm\bar{3}m$) structure [8].

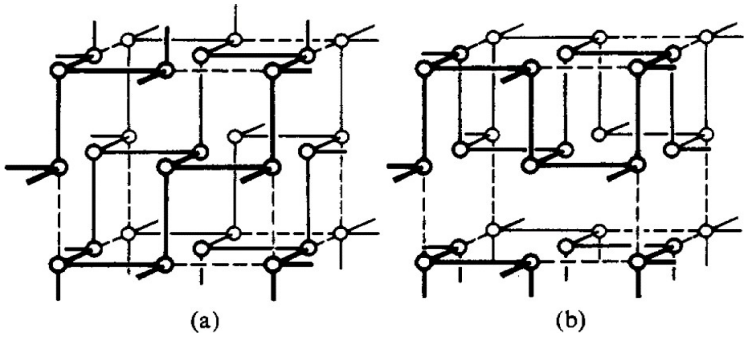

Figure 1. Relation of the structures of (a) gray As and (b) black P to the simple cubic structure [3].

Considering the structural and bonding scheme relationships between pnictogens (group 15 elements) and the binary interpnictogen compound (AsN), general conclusions on their atomic arrangements viewed as distorted parent simple cubic or rock salt structures will be drawn, in particular in light of the group–subgroup relationships of these topologically related crystal structures.

[1] Prewitt, C. T. & Downs, R. T. (1998). *Rev. Mineral.*, **37**, 283.
[2] Grochala, W., Hoffmann, R., Feng, J. & Ashcroft, N. W. (2007). *Angew. Chem. Int. Ed.,* **46**, 3620.
[3] Wells, A. F. (1975). *Structural Inorganic Chemistry*. London: Oxford University Press.
[4] Scelta, D., Baldassarre, A., Serrano–Ruiz, M., Dziubek, K., Cairns, A. B., Peruzzini, M., Bini, R. & Ceppatelli, M. (2017). *Angew. Chem. Int. Ed.,* **56**, 14135.
[5] Scelta, D., Baldassarre, A., Serrano-Ruiz, M., Dziubek, K., Cairns, A. B., Peruzzini, M., Bini, R. & Ceppatelli, M. (2018). *Chem. Commun*., **54**, 10554.
[6] Laniel, D., Winkler, B., Fedotenko, T., Pakhomova, A., Chariton, S., Milman, V., Prakapenka, V., Dubrovinsky, L. & Dubrovinskaia, N. (2020).
Phys. Rev. Lett., **124**, 216001.
[7] Ceppatelli, M., Scelta, D., Serrano-Ruiz, M., Dziubek, K., Morana, M., Svitlyk, V., Garbarino, G., Poręba, T., Mezouar, M., Peruzzini, M., & Bini, R. (2022). *Angew. Chem. Int. Ed.*, **61**, e202114191.
[8] Sukserm, A., Ceppatelli, M., Serrano-Ruiz, M., Scelta, D., Dziubek, K., Morana, M., Bini, R., Peruzzini, M., Bovornratanaraks, T., Pinsook, U. & Scandolo, S. (2024). *Inorg. Chem.*, **63**, 8142.