Angewandte Chemie

DOI: 10.1002/ange.201008070

Computational Chemistry

Ab Initio Energy Landscape of GeF_2: A System Featuring Lone Pair Structure Candidates

*Klaus Doll and Martin Jansen**

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

Each already known chemical configuration, as well as those that are stable but are still waiting to be experimentally discovered, corresponds to a minimum on the hyperspace of potential energy associated with the (chemical) configuration space. At finite temperatures, the configurations around such minimum structures are populated, constituting a "locally ergodic" region, corresponding to a macroscopic thermodynamic state, which can be addressed by the thermodynamic state functions G, H, and S. Since the structure of the potential energy landscape, and the locally ergodic regions present, are determined by natural laws, all chemical compounds and their structures are also predetermined. It follows that neither the composition, nor the structure, nor the properties of a specific chemical configuration is subject to external intervention, for example, by the synthetic chemist.[1]

Projecting the whole wealth of existing and not yet realized chemical configurations onto the related landscape of potential energy at 0 K, and the ergodic states of matter evolving at finite temperatures, is the foundation of our concept for targeted materials and solid-state syntheses.[2] In this picture, the first step of synthesis planning, namely predicting stable configurations that can serve as targets for synthesis, imposes the task of analyzing the energy landscape for local minima. Since even subsections of such a landscape cannot be computed by solving the Schrödinger equation for the ensembles of atoms to be realistically involved, one has to resort to the tools developed for the exploration of multiminima landscapes, for example, by scanning it using random walks. We have employed simulated annealing, in combination with steps according to the Monte Carlo method, using the total energy as the only cost function, and number and type of atoms, their positional vectors, and, most importantly, the lattice basis as parameters to be varied (move classes).[2] Meanwhile, several related approaches for the prediction of structures by global optimization have been introduced, among them molecular dynamics in various variants (e.g. metadynamics,[3] or a combination of molecular dynamics and path sampling[4]), genetic (evolutionary) algorithms,[5–8] or simply performing a local optimization, starting from random structures.[9] For overviews on structure prediction and energy landscapes, see, for example, references [2,10–12].

The shape of the energy landscape, as imaged by such a computational process, depends crucially on the quality and kind of the total energy calculations and to a lesser extent on the move classes applied, and will more or less deviate from the "true" landscape. Since the computational efforts to be made at exploring configuration spaces of significant size are huge, in the beginning, we based the total energy calculations on computationally "cheap" empirical two-body potentials.[2a–d] In spite of this approximation, the results have been quite promising, and the feasibility of the concept has been proven convincingly and validated experimentally at the example of the alkali metal nitrides[13–15] and the lithium halides.[16,17] However, the two-body potentials used, consisting of a Coulombic and a Lennard-Jones term, give predominantly ionic structures and are not suitable to address, for example, configurations containing homoatomic bonds. In particular, structures displaying electronically driven distortions would escape discovery at this level of total energy calculations. This drawback definitely challenges our ultimate objective of being able to predict stable configurations of any combination of the chemical elements. Therefore, at least for addressing systems in which homoatomic bonds are expected to occur, we have moved on to performing the total energy calculations on the ab initio level.[2f,18–21] The power of this further developed approach has been demonstrated by predicting new, interesting polymorphs of boron nitride.[19]

"Lone pair" electron configurations in combination with (partial) covalent bonding are known to induce conspicuously distorted coordination geometries. This effect of stereochemically active electron pairs continues to attract much attention throughout all fields of chemistry and physics.[22] The interest in such compounds in the field of solid-state chemistry originates mainly from the opportunities such systems might offer for pressure-enforced phase transitions, which are expected to trigger drastic changes in the physical properties, for example, from insulating to metallic or even superconducting behavior, including effects of multiferroicity.

We have regarded it a meaningful touchstone and challenge to investigate whether our approach of global searches on the ab initio level is able to (re)produce correct and reasonable structures showing lone pair effects without recourse to any preinformation. For such a case study, we chose GeF_2. Its structure at standard conditions is known.[23] An additional monoclinic phase, suggested to exist at 80 °C,[24] was, however, later questioned[25], and a tetragonal structure

---

[*] Prof. K. Doll, Prof. M. Jansen
Max Planck Institute for Solid State Research
Heisenbergstrasse 1, 70569 Stuttgart (Germany)
E-mail: M.Jansen@fkf.mpg.de
Prof. K. Doll
Institut für Mathematische Physik, TU Braunschweig
Mendelssohnstrasse 3, 38106 Braunschweig (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201008070.

with space group $P4_12_12$ (or its enantiomorph in space group $P4_32_12$) was proposed instead. Further germanium fluorides with known structure are GeF_4,[26] Ge_5F_{12},[27] and Ge_7F_{16}.[28]

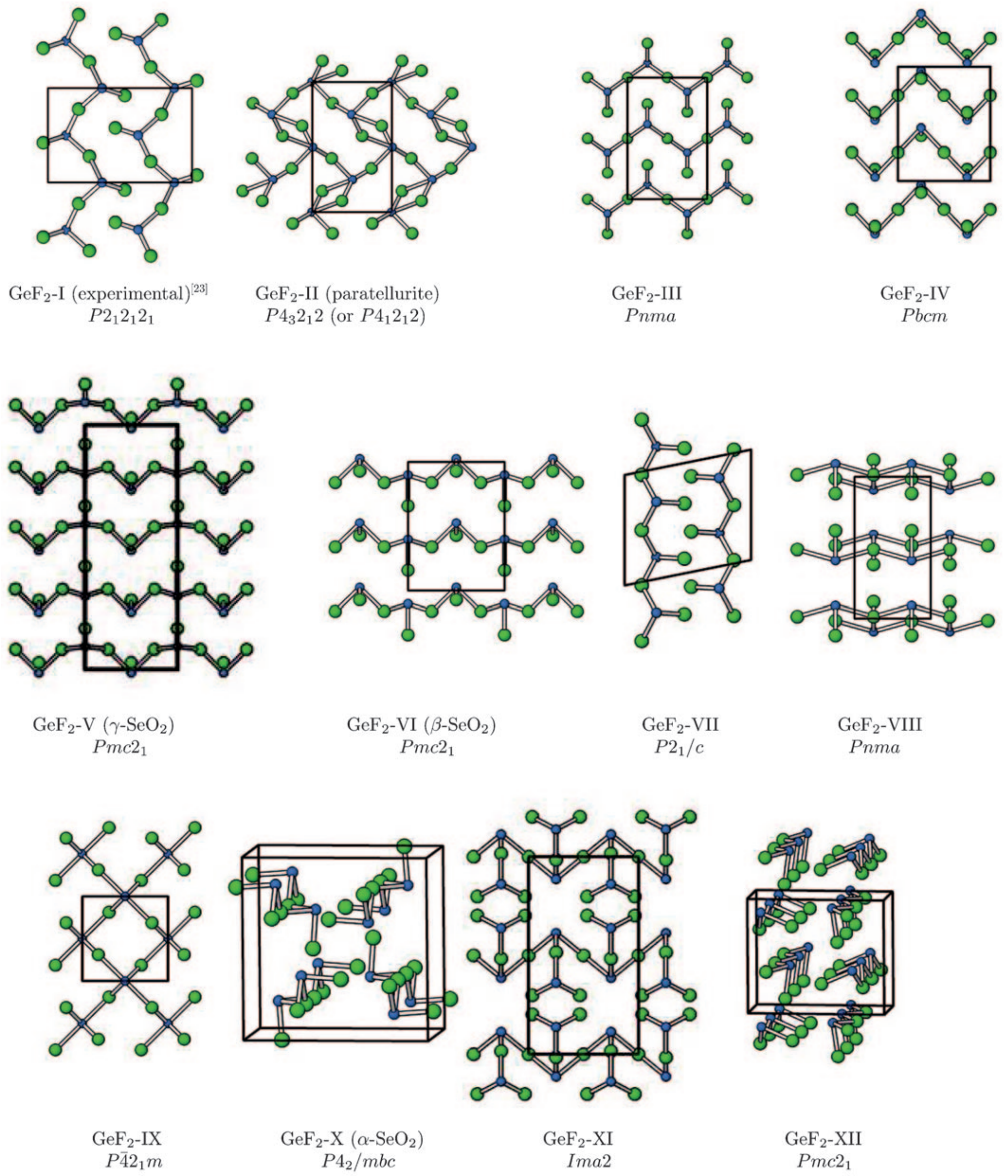
The general method consists of a global exploration based on simulated annealing with Monte Carlo steps, and subsequent local optimization. All the energies were computed on the ab initio level. It was found earlier,[19] and again in our case, that by using the Hartree–Fock approach, it is easiest to achieve convergence during the self-consistent field (SCF) procedure, because of the large band gaps on this level of theory, compared to, for example, the local density approximation (LDA). As van der Waals interactions were expected to play an important role, an additional empirical correction for such contributions[29] was added.

Since the global ab initio searches are quite expensive in computing time, it would be hard to come close to a complete exploration of the respective configuration space. Therefore, we added further potential candidates as start configurations for GeF_2: the structures of isoelectronic α-SeO_2,[30] β-SeO_2,[31] γ-SeO_2,[31] and β-TeO_2.[32]

The local optimization was performed with high accuracy, and on the level of various functionals: the LDA, the hybrid functional B3LYP, and the hybrid functional B3LYP in combination with an additional van der Waals term. The set of (meta)stable candidate structures, as obtained after the local optimization, is displayed in Figure 1 in the sequence of increasing total energies. The respective data are given in Table 1 together with the total energies. The full structural information (including the fractional coordinates) is given in Table S1 in the Supporting Information.

As an important, and most pleasing result, our global search of the ab initio energy landscape of GeF_2 has by far prevailingly tracked stable configurations featuring first coordination spheres that are characteristically crooked, indicating the presence of a stereochemically active lone pair. Furthermore, most of the structure candidates identified display covalently bonded chainlike substructures that are held together by interchain van der Waals and F→Ge donor–acceptor bonds.

Figure 2 gives a schematic representation of the primary building blocks and their connectivities, as revealed by the global searches. The linkages of the coordination polyhedra around germanium need to comply with the overall composition, and can easily be expressed by the respective Niggli[33] formulae: $\mathrm{GeF}_{2/2}\mathrm{F}_{1/1}$ (a), $\mathrm{GeF}_{4/2}$ (b), $[\mathrm{GeF}_{3/2}; \mathrm{GeF}_{1/2}\mathit{F}_{2/1}]$ (c,d), and $\mathrm{GeF}_{2/1}$ (e). It should be noted that by using the primary building units (a), (b), and (e) alone, the correct composition can be achieved, whereas configurations (c) and (d) need to be combined in a 1:1 ratio.


GeF_2-I (experimental)[23] $P2_12_12_1$

GeF_2-II (paratellurite) $P4_32_12$ (or $P4_12_12$)

GeF_2-III $Pnma$

GeF_2-IV $Pbcm$

GeF_2-V (γ-SeO_2) $Pmc2_1$

GeF_2-VI (β-SeO_2) $Pmc2_1$

GeF_2-VII $P2_1/c$

GeF_2-VIII $Pnma$

GeF_2-IX $P\bar{4}2_1m$

GeF_2-X (α-SeO_2) $P4_2/mbc$

GeF_2-XI $Ima2$

GeF_2-XII $Pmc2_1$

Figure 1. Graphical representations of the twelve most stable structure candidates encountered for GeF_2 (see Table 1).

Table 1: Space groups, cell parameters, and total energies of the energetically most favorable structures found during the global searches of the energy landscape of GeF_2.[a]

Modification and space group	Cell parameters [in Å and °], volume [in Å^3], and energy [in E_h per four formula units]			
	LDA	B3LYP	B3LYP + dispersion	experiment
GeF_2-I as in Ref. [23] $P2_12_12_1$	$a=4.27$, $b=5.19$, $c=7.60$ $V=168.35$ -809.4802	$a=5.25$, $b=5.12$, $c=8.12$ $V=217.82$ -814.1942	$a=4.29$, $b=5.24$, $c=8.09$ $V=181.62$ -814.2871	$a=4.682$, $b=5.178$, $c=8.312$ $V=201.51$, Ref. [23]
GeF_2-II (α-TeO_2) $P4_32_12$ (or the enantiomorph in space group $P4_12_12$)	$a=4.78$, $c=7.65$ $V=175.06$ -809.4786	$a=5.17$, $c=8.14$ $V=217.58$ -814.1940	$a=4.83$, $c=8.00$ $V=186.96$ -814.2838	$a=4.853$, $c=8.579$ $V=202.05$, Ref. [25]
GeF_2-III *Pnma*	$a=7.80$, $b=5.22$, $c=4.10$ $V=166.85$ -809.4703	$a=8.58$, $b=5.45$, $c=4.69$ $V=219.41$ -814.1904	$a=8.35$, $b=5.40$, $c=4.12$ $V=185.86$ -814.2838	
GeF_2-IV *Pbcm*	$a=5.53$, $b=6.24$, $c=5.08$ $V=175.10$ -809.4646	$a=6.20$, $b=6.53$, $c=5.49$ $V=222.31$ -814.1886	$a=5.13$, $b=6.73$, $c=5.50$ $V=189.88$ -814.2791	
GeF_2-V (γ-SeO_2) $Pmc2_1$ based on Ref. [31]	$a=5.37$, $b=4.28$, $c=14.83$ $V=170.46$ -809.4703	$a=5.64$, $b=4.67$, $c=17.37$ $V=228.67$ -814.1875	$a=5.60$, $b=4.54$, $c=14.99$ $V=190.20$ -814.2751	
GeF_2-VI (β-SeO_2) $Pmc2_1$ based on Ref. [31]	$a=5.39$, $b=4.26$, $c=7.45$ $V=170.84$ -809.4698	$a=5.63$, $b=4.68$, $c=8.66$ $V=227.86$ -814.1871	$a=5.58$, $b=4.59$, $c=7.54$ $V=193.09$ -814.2749	
GeF_2-VII $P2_1/c$	$a=7.15$, $b=3.48$, $c=7.58$ $\beta=119.4°$ $V=164.26$ -809.4578	$a=6.33$, $b=6.26$, $c=5.83$ $\beta=97.9°$ $V=228.38$ -814.1895	$a=6.77$, $b=4.80$, $c=5.87$ $\beta=101.5°$ $V=187.13$ -814.2686	
GeF_2-VIII *Pnma*	$a=6.04$, $b=3.60$, $c=7.37$ $V=160.07$ -809.4697	$a=6.59$, $b=3.72$, $c=8.29$ $V=203.20$ -814.1586	$a=5.50$, $b=4.21$, $c=7.92$ $V=183.30$ -814.2651	
GeF_2-IX $P\bar{4}2_1m$	$a=4.99$, $c=4.06$ $V=202.03$ -809.4590	$a=5.19$, $c=4.46$ $V=239.76$ -814.1920	$a=5.03$, $c=4.25$ $V=214.71$ -814.2650	
GeF_2-X (α-SeO_2) $P4_2/mbc$ based on Ref. [30]	$a=8.27$, $c=5.44$ $V=185.82$ -809.4593	$a=9.22$, $c=5.67$ $V=240.54$ -814.1829	$a=8.73$, $c=5.64$ $V=214.90$ -814.2650	
GeF_2-XI *Ima*2	$a=5.91$, $b=12.00$, $c=4.98$ $V=176.55$ -809.4692	$a=6.14$, $b=12.48$, $c=5.94$ $V=227.57$ -814.1869	$a=6.10$, $b=11.10$, $c=5.88$ $V=198.83$ -814.2631	
GeF_2-XII $Pmc2_1$	becomes GeF_2-VIII	$a=3.63$ $b=7.98$ $c=7.15$ $V=207.06$ -814.1611	$a=3.62$ $b=7.65$ $c=6.50$ $V=180.03$ -814.2535	
GeF_2-XIII fluorite $Fm\bar{3}m$	$a=5.49$ $V=165.85$ -809.4532	$a=5.61$ $V=176.91$ -814.1120	$a=5.54$ $V=170.13$ -814.2047	

[a] Total energy given per four formula units in Hartree units; 1 $E_h=27.2114$ eV $=2625.5$ kJ mol^{-1}. Structures are listed in the sequence of increasing energy on the level of B3LYP + dispersion. Fractional coordinates are given in Table S1 in the Supporting Information.

In terms of qualitative concepts, the individual bond lengths and angles can be fully rationalized by the local valence electron distributions (VSEPR concept[34]) and by the 3D connectivities. All structure candidates predicted, except for the fluorite structure, display stereochemically active nonbonding electron pairs. As expected, the Ge–F bond lengths are significantly shorter for the terminal than for the linking fluorine atoms, and further individual variations can

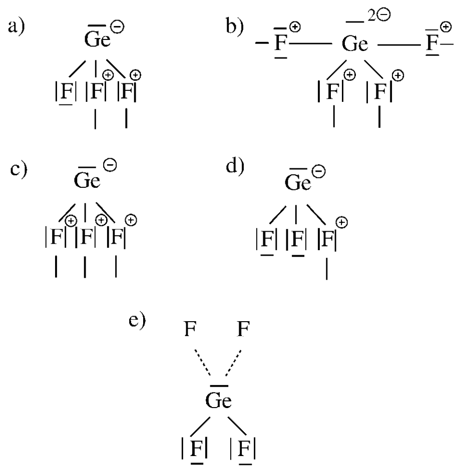


Figure 2. Types of primary building blocks as encountered during the global exploration of the GeF$_2$ ab initio energy landscape. The presentation according to the Lewis formalism includes formal charges for the sake of bookkeeping valence electrons. They are physically meaningless.[44]

well be understood in terms of slight changes in the respective neighborhoods.

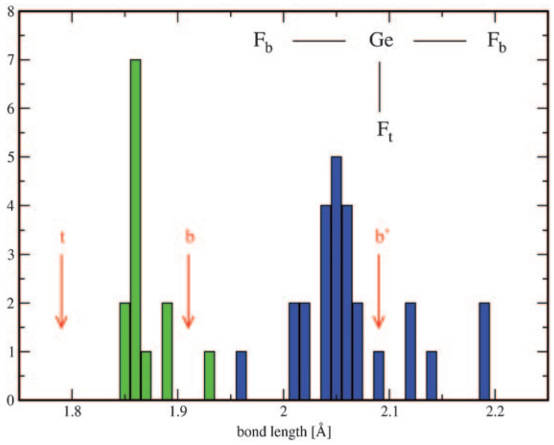


Figure 3. Statistics of the computed bond lengths for the ensemble of structures with Niggli formula GeF$_{2/2}$F$_{1/1}$ (green: terminal bonds, blue: bridging bonds). Arrows indicate the experimentally measured bond lengths (t = terminal, b = bridging). For details on the bond lengths and angles, see Table S2 in the Supporting Information.

As an example for the local configuration (a) in Figure 2, the distribution of the Ge–F bond lengths is displayed in Figure 3, and the corresponding bond lengths and angles are listed in Table S2 in the Supporting Information. Among the structures showing such a local configuration are the experimentally observed one (GeF$_2$-I), and furthermore GeF$_2$-III, GeF$_2$-IV, GeF$_2$-V (γ-SeO$_2$), GeF$_2$-VI (β-SeO$_2$), GeF$_2$-VII, GeF$_2$-X (α-SeO$_2$), and GeF$_2$-XII (labels are as in Figure 1). In the computationally generated structures, the bond lengths from germanium to terminal fluorine atoms range from 1.85 to 1.93 Å, and the bridging bonds are in the range from 1.96 to 2.19 Å. The spread of both classes of bonds, the terminal and the bridging ones, is quite wide. Even these features can be well understood in terms of secondary bonding. For example, in GeF$_2$-I, the Ge–F$_b$–Ge′ bridge was found to be considerably asymmetric with Ge–F$_b$ = 1.96 (experimental structure: 1.91) Å and Ge′–F$_b$ = 2.14 (2.09) Å. This striking difference is related to a kind of *trans* effect caused by a terminal fluorine atom from the adjacent chain, approaching Ge′ to a distance of 2.46 (2.57) Å virtually opposite to F$_b$. We regard it noteworthy that the experimentally found spectrum of distances with all its subtle differentiations was reproduced computationally without using any heuristic input.

In addition to the connectivities corresponding to the primary building block (a) in Figure 2, which are by far the most common, some more “exotic”, but chemically and physically meaningful configurations have also been identified. One (GeF$_2$-XI) can be addressed by the Niggli formula GeF$_{3/2}$GeF$_{2/1}$F$_{1/2}$, which indicates the presence of two germanium atoms of different structural function. Also, there are the extremes of virtually molecular GeF$_2$ units (GeF$_2$-VIII, Niggli formula GeF$_{2/1}$), or of a Ge–F network including exclusively bridging fluorine atoms (GeF$_{4/2}$). The latter is realized in GeF$_2$-II, which is isostructural with α-TeO$_2$, and in GeF$_2$-IX, which is made of GeF$_2$ layers.

For the synthetic chemist, it is sufficient to know whether a given configuration corresponds to a minimum region on the energy landscape, indicating that it is at least kinetically stable. The absolute values and their accuracies are thus less relevant in the context of our approach to synthesis planning.[2] However, accordance of experimental and computed quantities constitute a valuable measure for the overall reliability of the results achieved. Again, it is satisfying that the lowest total energy configuration found corresponds to the experimentally known one. However, a comparison of calculated and experimental results with respect to lattice constants, as well as bonding distances, reveals considerable discrepancies (see Tables S1 and S2 in the Supporting Information), even among those calculated just with different methods and functionals. For example, in the experimental structure, the Ge–F–Ge chain extends along the *b* axis with the lattice basis chosen as given in Table 1. The chains interact only weakly in the crystallographic *a* direction, and the deviations of the computed values of *a* from the experimentally measured one are relatively large: 4.27 Å at the level of the LDA (−9 % compared to the experimental value of 4.682 Å), 5.25 Å at the B3LYP level (+12 %), and 4.29 Å at the level of B3LYP + dispersion (−8 %). Similar deviations were also found for the computed length of the *c* lattice constant. The length of *b* is least sensitive with respect to the method used, which appears reasonable, since *b* is in the direction of the chains and its length is mainly determined by covalent bonds. As can be seen by comparing the results (B3LYP and B3LYP with dispersion), the dispersion has a significant effect on the optimized geometry of the 3D arrangement of the chainlike substructures. The deviations discussed thus appear to be mainly due to the difficulty in treating dispersion adequately. Of the three methods employed, the best agreement with experimental results was obtained with B3LYP + dispersion. A proper treatment of the dispersion interaction in solids is presently an active research field, and besides employing an empirical dispersion term,[29] there are suggestions such as employing the random phase approximation[35] or second-order perturbation theory.[36,37]

Addressing the germanium(II) fluoride system computationally has posed particular challenges, for example, treating the electron lone pair and the highly mutable bonding schemes involved, as there are strong covalent Ge$-$F$_t$, significantly weaker Ge$-$F$_b$, or soft Ge$\leftarrow$F donor bonds, the latter together with van der Waals interactions effecting the bonding between the $^{1}_{\infty}$GeF$_2$ chains. Given this complexity, the results obtained are convincing: the experimentally known facts have been reliably reproduced and definitely meaningful new targets for synthesis have been suggested. This is a further proof for the conclusiveness and feasibility of our concept for solid-state and materials synthesis planning. In particular, the study presented herein convincingly demonstrates the high level of universality achieved in analyzing realistic and complex chemical systems with respect to predicting all (meta)stable compounds and their structures without any recourse to a priori information. This approach will give substantial impetus to future solid-state and materials synthesis, in particular in making this endeavor more targeted and efficient.

Experimental Section

Methods: The main set of simulated annealing calculations was performed with four formula units of GeF$_2$. These 12 atoms were initially put in random positions in a cubic box with an edge length of 11 Å without using symmetry, that is, in space group *P*1. A simulated annealing run had a length of 50000 steps, followed by 15000 quench steps. In total, 170 such runs were performed. The raw structures obtained were subjected to a symmetry analysis with KPLOT.[38]

The ab initio calculations were run with the CRYSTAL09 code,[39] which is based on local Gaussian-type orbitals. Two different levels of accuracy were applied. The energy calculations during the simulated annealing part consumed the bulk of the CPU time and had to be done as efficiently as possible. The subsequent local optimizations were based on analytical gradients with respect to the atom positions,[40] the cell parameters,[41] and the optimizer.[42] These calculations were done on a higher level of accuracy. The germanium and fluorine basis sets were modifications of earlier published ones.[43] Full details can be found in the Supporting Information.

Received: December 21, 2010
Published online: April 14, 2011

Keywords: ab initio calculations · lone pairs · solid-state structures · structure elucidation

---

[1] M. Jansen, J. C. Schön, *Angew. Chem.* **2006**, *118*, 3484; *Angew. Chem. Int. Ed.* **2006**, *45*, 3406.
[2] a) J. C. Schön, M. Jansen, *Angew. Chem.* **1996**, *108*, 1358; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1286; b) M. Jansen, *Angew. Chem.* **2002**, *114*, 3896; *Angew. Chem. Int. Ed.* **2002**, *41*, 3746; c) J. C. Schön, M. Jansen, *Z. Kristallogr.* **2001**, *216*, 307; d) J. C. Schön, M. Jansen, *Z. Kristallogr.* **2001**, *216*, 361; e) J. C. Schön, M. Jansen, *Int. J. Mater. Res.* **2009**, *100*, 135; f) J. C. Schön, K. Doll, M. Jansen, *Phys. Status Solidi B* **2010**, *247*, 23; g) M. Jansen, K. Doll, J. C. Schön, *Acta Crystallogr. Sect. A* **2010**, *66*, 518.
[3] R. Martonak, A. Laio, M. Parrinello, *Phys. Rev. Lett.* **2003**, *90*, 075503.
[4] D. Zahn, S. Leoni, *Phys. Rev. Lett.* **2004**, *92*, 250201.
[5] S. Woodley, P. D. Battle, J. D. Gale, C. R. A. Catlow, *Phys. Chem. Chem. Phys.* **1999**, *1*, 2535.
[6] A. R. Oganov, C. W. Glass, *J. Chem. Phys.* **2006**, *124*, 244704.
[7] N. L. Abraham, M. I. J. Probert, *Phys. Rev. B* **2006**, *73*, 224104.
[8] G. Trimarchi, A. Zunger, *Phys. Rev. B* **2007**, *75*, 104113.
[9] a) C. J. Pickard, R. J. Needs, *Phys. Rev. Lett.* **2006**, *97*, 045504; b) C. J. Pickard, R. J. Needs, *J. Phys. Condens. Matter* **2011**, *23*, 053201.
[10] S. M. Woodley, C. R. A. Catlow, *Nat. Mater.* **2008**, *7*, 937.
[11] D. J. Wales, *Energy Landscapes*, Cambridge University Press, Cambridge, **2003**.
[12] “Applications of Evolutionary Computation in Chemistry”: *Structure and Bonding*, *Vol. 110* (Ed.: R. L. Johnston), Springer, New York, **2004**.
[13] J. C. Schön, M. Wevers, M. Jansen, *J. Mater. Chem.* **2001**, *11*, 69.
[14] D. Fischer, M. Jansen, *Angew. Chem.* **2002**, *114*, 1831; *Angew. Chem. Int. Ed.* **2002**, *41*, 1755.
[15] G. V. Vajenine, X. Wang, I. Efthimiopoulos, S. Karmakar, K. Syassen, M. Hanfland, *Phys. Rev. B* **2009**, *79*, 224107.
[16] J. C. Schön, M. Jansen, *Comput. Mater. Sci.* **1995**, *4*, 43; Ž. Čančarević, J. C. Schön, M. Jansen, *Chem. Asian J.* **2008**, *3*, 561.
[17] a) Y. Liebold-Ribeiro, D. Fischer, M. Jansen, *Angew. Chem.* **2008**, *120*, 4500; *Angew. Chem. Int. Ed.* **2008**, *47*, 4428; b) A. Bach, D. Fischer, M. Jansen, *Z. Anorg. Allg. Chem.* **2009**, *635*, 2406.
[18] K. Doll, J. C. Schön, M. Jansen, *Phys. Chem. Chem. Phys.* **2007**, *9*, 6128.
[19] K. Doll, J. C. Schön, M. Jansen, *Phys. Rev. B* **2008**, *78*, 144110.
[20] K. Doll, J. C. Schön, M. Jansen, *J. Chem. Phys.* **2010**, *133*, 024107.
[21] A. Kulkarni, K. Doll, J. C. Schön, M. Jansen, *J. Phys. Chem. B* **2010**, *114*, 15573.
[22] a) R. E. Dinnebier, S. Carlson, M. Hanfland, M. Jansen, *Am. Mineral.* **2003**, *88*, 996; b) M. W. Stoltzfus, P. M. Woodward, R. Seshadri, J.-H. Klepeis, B. Bursten, *Inorg. Chem.* **2007**, *46*, 3839; c) S. Ghedia, T. Locherer, R. Dinnebier D. L. V. K. Prasad, U. Wedig, M. Jansen, A. Senyshyn, *Phys. Rev. B* **2010**, *82*, 024106.
[23] J. Trotter, M. Akhtar, N. Bartlett, *J. Chem. Soc. A* **1966**, *58*, 200.
[24] G. P. Adams, L. M. Albritton, D. W. Bonnell, J. L. Margrave, J. Scott, P. W. Wilson, *J. Less-Common Met.* **1971**, *24*, 113.
[25] G. Denes, *J. Solid State Chem.* **1989**, *78*, 52.
[26] J. Köhler, A. Simon, R. Hoppe, *J. Less-Common Met.* **1988**, *137*, 333.
[27] J. C. Taylor, P. W. Wilson, *J. Am. Chem. Soc.* **1972**, *95*, 1834.
[28] J. Köhler, J.-H. Chang, *Z. Anorg. Allg. Chem.* **1997**, *623*, 596.
[29] S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787.
[30] K. Stahl, J. P. Legros, J. Galy, *Z. Kristallogr.* **1992**, *99*, 202.
[31] D. Orosel, O. Leynaud, P. Balog, M. Jansen, *J. Solid State Chem.* **2004**, *177*, 1631.
[32] H. Beyer, K. Sahl, J. Zemann, *Naturwissenschaften* **1965**, *52*, 155.
[33] P. Niggli, *Grundlagen der Stereochemie*, Birkhäuser, Basel, **1945**.
[34] R. J. Gillespie, E. A. Robinson, *Chem. Soc. Rev.* **2005**, *34*, 396.
[35] J. Harl, L. Schimka, G. Kresse, *Phys. Rev. B* **2010**, *81*, 115116.
[36] M. Halo, S. Casassa, L. Maschio, C. Pisani, R. Dovesi, D. Ehinon, I. Baraille, M. Rérat, D. Usvyat, *Phys. Chem. Chem. Phys.* **2011**, *13*, 4434.
[37] A. Tkatchenko, L. Romaner, O. T. Hofmann, E. Zojer, C. Ambrosch-Draxl, M. Scheffler, *MRS Bull.* **2010**, *35*, 435.
[38] R. Hundt, KPLOT, University of Bonn, Germany, **1979**; Version 9, **2007**.
[39] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D’Arco, M. Llunell, *CRYSTAL2009*, University of Torino, Torino, **2009**.

[40] a) K. Doll, V. R. Saunders, N. M. Harrison, *Int. J. Quantum Chem.* **2001**, *82*, 1; b) K. Doll, *Comput. Phys. Commun.* **2001**, *137*, 74.

[41] a) K. Doll, R. Dovesi, R. Orlando, *Theor. Chem. Acc.* **2004**, *112*, 394; b) K. Doll, R. Dovesi, R. Orlando, *Theor. Chem. Acc.* **2006**, *115*, 354; c) K. Doll, *Mol. Phys.* **2010**, *108*, 223.

[42] B. Civalleri, P. D'Arco, R. Orlando, V. R. Saunders, R. Dovesi, *Chem. Phys. Lett.* **2001**, *348*, 131.

[43] a) A. Bergner, M. Dolg, W. Küchle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431; b) R. Nada, C. R. A. Catlow, C. Pisani, R. Orlando, *Modell. Simul. Mater. Sci. Eng.* **1993**, *1*, 165; c) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213.

[44] M. Jansen, U. Wedig, *Angew. Chem.* **2008**, *120*, 10176; *Angew. Chem. Int. Ed.* **2008**, *47*, 10026.