



**HAL**  
open science

# How high pressure can be involved in chemical bonding

Gérard Demazeau

► **To cite this version:**

Gérard Demazeau. How high pressure can be involved in chemical bonding. Defect and Diffusion Forum, 2002, 208-209, pp.85-91. 10.4028/www.scientific.net/DDF.208-209.85 . hal-00818888

**HAL Id: hal-00818888**

**<https://hal.science/hal-00818888>**

Submitted on 7 Jul 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# How High Pressures can be Involved in Chemical Bonding

Gérard Demazeau

Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-UPR.CNRS-9048),  
87 Av. A. Schweitzer, FR-33608 Pessac Cedex, France

and

Interface Hautes Pressions (ENSCP-ICMCB), Ecole Nationale Supérieure de Chimie et de  
Physique de Bordeaux, 161 Avenue Pey-Berland, FR-33608 Pessac Cedex, France

**Keywords:** Chemical Bonding, Electronic Phenomena, High Pressures, Structural Transformation, Synthesis

**Abstract.** In a first approach, between two atoms A and B, two different types of chemical bonds can be possibly involved : (i) a strong with electronic exchange, (ii) a weak involving electrostatic or Van der Waals interactions.

In both cases the interatomic distance A-B is an important parameter.

Physics, Solid State Chemistry, Materials Sciences and Co-ordination Chemistry involve mainly strong bonds, on the contrary in Biosciences weak bonds play an important role (conformation of the molecules...).

Two approaches can be used for evaluating the pressure effects on chemical bonds.

(i) The chemical bond exists and, in such a case, pressure leads to a decrease of the average distance A-B inducing mainly electronic and steric phenomena.

(ii) How high pressures can help the formation of a chemical bond between two atoms A and B and then induce the synthesis of new compounds ?

Physics and Biosciences are mainly involved in the first approach with for Physics the study of the structural transformations and/or the electronic phenomena (charge transfer, disproportionation, electronic delocalization...).

In the case of Biosciences the pressure effects on the weak bonds are very important either on the kinetics or the deformation of the molecules.

In Solid State Chemistry and Materials Sciences, the induction of new chemical bonding is important for preparing functional materials.

Co-ordination chemistry involves both approaches.

Due to the fact that chemical bonding is an important factor for describing the research activity of different domains (Physics, Solid State Chemistry, Materials Science, Co-ordination Chemistry, Biosciences...), High Pressures appear as a fruitful tool either for the modification of existing systems or for the synthesis of new ones.

## Introduction

Two types of chemical bonds can be considered :

- the strong bonds involving the exchange of electrons (covalent bond as the C-C bond in diamond, ionic bond as in NaCl and metallic bond as Cu-Cu in copper metal...),
- the weak bonds without exchange of electrons as Van der Waals bond and electrostatic bond (observed in water as so-call "hydrogen-bond").

In both cases the A-B distance characterizing the chemical bond is important. If Solid State Chemistry involves mainly strong bonds, Organic Chemistry, Coordination Chemistry and Biochemistry are mainly concerned both with strong but also weak bonds. In such cases weak bonds can play a specific role (conformation of the molecule, solvation...).

## I) INFLUENCE OF HIGH PRESSURE ON CHEMICAL BONDS.

Chemical bonds can be involved in two types of systems :

- extended systems with either a long distance ordering (crystallized compounds) or a short distance ordering (amorphous systems),
- limited systems observed mainly in molecular chemistry :
  - organic chemistry,
  - coordination chemistry,
  - biochemistry.

Two different approaches can be used for evaluating the high pressure effects on chemical bonding :

- the chemical bond exists and what are the main effects induced by high pressures ?
- what is the role of high pressure for improving the formation of chemical bonds and consequently the role of pressure on the synthesis of materials ?

## II) HIGH PRESSURE EFFECTS ON EXISTING CHEMICAL BONDS.

The main pressure effect on the chemical bond is, versus its compressibility, the decrease of the A-B distance ( $d$ ).

If we consider a general diagram giving the energy  $E$  versus the A-B distance, if  $d$  is lower than the critical distance  $d_c$  (corresponding to the lowest energy) high pressures can induce a destabilization phenomenon. (Fig. 1)

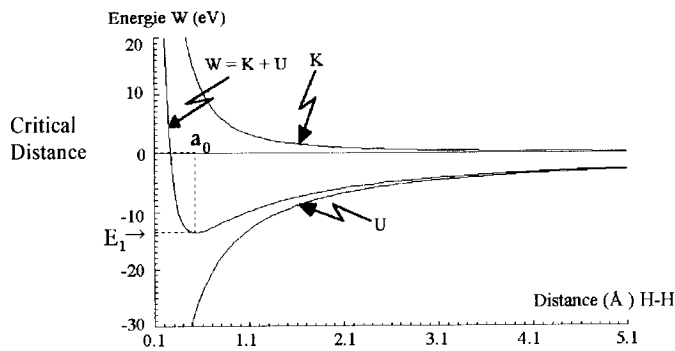
Such a destabilization is mainly due to strong electrostatic repulsion.

Versus the extension of system two different types of phenomena can be induced.

- (i) In an extended systems, in Solid State Chemistry, in order to minimize the electronic repulsion an electronic transition : insulator→metal can be induced. For example the insulator → metal transition has been observed for  $\text{Sr}_3\text{Fe}_2\text{O}_7$  in a pressure range close to 28 - 30 GPa. [1].
- (ii) In a limited system, as a complex in Coordination Chemistry or in an extended system, the pressure effects leads to an increase of the local crystal field energy ( $10Dq$ )

implying a change of the electronic configuration (from the high spin to the low-spin state) with a decrease of the number of electrons localized in the  $d$  orbitals oriented towards the ligands.

M. TAKANO et al. have pointed out a change of electronic configuration induced by high pressure for  $\text{Fe}^{4+}$  in the perovskite lattice  $\text{CaFeO}_3$ . [2]



**Fig. 1** : Evolution of the energy vs. the (H-H) distance for the formation of H<sub>2</sub>

In some cases a competition can take place between two electronic phenomena [3] :

- the local charge transfer leading to the modification of the formal oxidation state of the transition metal,
- the co-operative change of the electronic configuration : high spin → low spin.

→ Another important electronic phenomenon correlated with the decrease of the A-B distance is the charge transfer. Such a charge transfer phenomenon can also participate to the formation of new chemical bonds. Such a phenomenon has been observed for GeI<sub>4</sub>. [4]

→ The application of high pressure on extended systems can lead to structural transitions induced by the reduction of the electrostatic or/and steric repulsion accompanying the decrease of the interatomic distance.

One of the most illustrative examples of electrostatic repulsions induced by high pressures is the structural transformations of ABX<sub>3</sub> polytypes with the hexagonal perovskite structure.

Due to the compressibility, the B-B distance decreases and consequently share-face octahedra are transformed continuously with increasing pressure to share-corner octahedra leading to the following sequence : 2H → 9H → 6H → 3C. [5]

A combination of electrostatic and steric repulsions induces the structural transformations in the Li<sub>2</sub>MF<sub>6</sub> fluorides (M<sup>4+</sup>=Ge, Ti, Zr). In such a case, if the M<sup>4+</sup>M<sup>4+</sup> distance remains approximately constant, the number of common edge between (MF<sub>6</sub>) and (LiF<sub>6</sub>) octahedra decreases when the size of M<sup>4+</sup> increases or under high pressures for a constant M<sup>4+</sup> cation. [6]

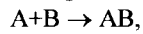
In some specific cases, anionic repulsions induced by high pressures can lead to structural transformations, this is the case for K<sub>2</sub>M<sup>4+</sup>O<sub>3</sub>. [7]

→ Another phenomenon induced by high pressures is a transition from a long-distance ordering to the short-distance one leading to the amorphization. [8]

### III) HIGH PRESSURE AND THE IMPROVEMENT OF THE FORMATION OF CHEMICAL BONDS.

#### III-1. Synthesis of new materials through densification effect.

As a general rule, if we consider the following equation :



if A,B and AB are solids, pressure can help the AB synthesis if :

$$V_A/Z_1 + V_B/Z_2 < V_{AB}/Z_3,$$

Where  $V_A/Z_1$ ,  $V_B/Z_2$  and  $V_{AB}/Z_3$  represent respectively the volume per unit formula for these three materials.

If  $V_{AB}/Z_3 < V_A/Z_1 + V_B/Z_2$  high pressures favour the synthesis of the AB compound.

Such a condensation effect can help the synthesis of new compounds unknown at normal pressure conditions. This is in particular the case in the system  $Al_2O_3 - B_2O_3$ . At room pressure two ternary compounds can be prepared with the following compositions :  $9Al_2O_3 - 2B_2O_3$  and  $2Al_2O_3 - B_2O_3$ . At 4GPa, studying the same  $Al_2O_3 - B_2O_3$  diagram the previous compositions are not observed but two new compounds  $Al_3BO_6$  and  $AlBO_3$  have been identified. [9]

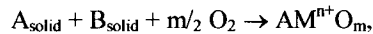
Consequently it appears that high pressures can modify drastically phase-diagrams through the promotion of the denser lattices.

#### III-2 Synthesis of new materials using precursors with different physico-chemical properties.

At normal pressure it is very often difficult to get intermediate compounds using precursors with very different physico-chemical properties (melting temperatures, vapor pressure...). Using high pressures it is possible, in Solid State Chemistry, to improve the reactivity. Consequently new compositions can be obtained if densities are bigger than the density of the corresponding stoichiometries of precursors. This is the case of oxifluorides as  $KTiO_2F$  [10] or  $Tl^+Tl^{3+}OF_2$ . [11]

#### III-3. Stabilization of the highest oxidation states of transition metals.

The synthesis of an oxide can be summarized by the following equation :



$$\text{With } \Delta G = \Delta G^\circ - m/2RT \log PO_2.$$

Consequently the use of oxygen pressures can help the stabilization of unusual  $n+$  formal oxidation states. [12]

The interest of such new  $M^{n+}O$  chemical bond is the strong improvement of the covalency, the M-O bond with the increase of the  $n+$  value. This improvement is higher than that induced by higher pressures on a  $M^{n+}O$  bond with a constant  $n+$  value due to the small compressibility of solids.

During these last thirty years - different unusual oxidation states of transition metals as Fe(IV) [13, 14], Fe(V) [15], Co(III) [16], Co(IV) [17], Ni(III) [18], Cu(III) [19] have been stabilized.

The main interest of such  $M^{n+}O$  is the study of electronic phenomena induced by the strong covalency as : charge transfer, low spin  $\rightarrow$  high spin transition, insulator  $\rightarrow$  metal transition, disproportionation....

#### III-4. The stabilization of strong covalent bonds between light elements.

The exceptional physico-chemical properties of diamond are mainly induced by the strong covalency of the C-C bonds and the directionality of these bonds ( $sp^3$  hybridization for carbon). [20]

High pressures have been particularly used for preparing new materials with light elements B,C,N,O....

The first success was the first synthesis of the cubic form of boron nitride (c-BN) [21].

During these last years three main research axes have been developed :

- (i) the study of the solid solution between diamond and c-BN [22, 23],
- (ii) the preparation of boron sub-oxides in order to evaluate the B-O bonds (24, 25),
- (iii) the stabilization of carbon nitrides, in particular the three dimensional forms of  $C_3N_4$ , the shorter C-N bond ( $d = 1047 - 1.49 \text{ \AA}$ ) than the C-C ones ( $d = 1.54 \text{ \AA}$ ) being able to induce physico-chemical properties comparable to that of diamond. [26-30]

#### III-5. The synthesis of new materials through the stabilization of thermally unstable precursors.

If the decomposition temperature ( $T_D$ ) or the sublimation temperature ( $T_S$ ) of precursors is smaller than the reaction temperature required for the synthesis, high pressures can help the preparation of new materials through the thermal stabilization of the precursors.

Such an application of high pressures has been developed for preparing oxides from  $H_2O$  [31, 32],  $MnO_2$  or  $PbO_2$  as precursors. This development leads to study the influence of the M-O chemical bond ( $M = Hg^{2+}, Mn^{4+}, Pb^{4+} \dots$ ) on the electronic properties of the resulting oxides as for examples  $Ln_2 Mn_2 O_7$  [33] or  $Ln_2 Pb_2 O_7$ . [34]

#### III-6. Influence of the compressibility of atoms on the stabilization of new compounds.

The synthesis of a compound  $A_x B_y X_z$  depends on a specific structure and consequently the co-ordination adopted by A and B. The co-ordination number being dependent on the  $r_A/r_X$  and the  $r_B/r_X$  ratio.

In situ, under high pressure conditions, the compressibility of A and B can play an important role in the synthesis of the resulting  $A_x B_y X_z$  compound.

The compressibility of atoms can be correlated to their electronic structures. Such a phenomenon has been used for extending the stability domain of some structures as the pyrochlore structure for the  $Ln_2 Ge_2^{4+} O_7$  compounds. [35]

### **III-7. The "in situ" modification of the electronic structure of atoms and the synthesis of new materials.**

The electronic structure of an atom depends closely on the respective energies of the orbitals. For the alkaline elements the energy of the external orbitals under high pressures conditions increases more drastically than that of the d orbitals.

Consequently using high pressures it is possible "in situ" to modify the electronic population of the orbitals with a s → d transition inducing a new chemical behaviour. For example at normal pressure conditions if no reaction occurs between K and Ni under high pressure conditions, it is possible to prepare K-Ni intermetallic compounds. [36-38]

### **III-8. Improvement of the chemical reactivity.**

Using solvent under supercritical or near supercritical conditions, it is possible - due to the modifications of the specific physico-chemical properties - to modify strongly the reactivity.

Reactions involving such conditions are called "Solvothetical Reactions" and are used for inducing the formation of chemical bonds :

- synthesis of new materials,
- sintering at medium temperature.

The development of such reactions will improve chemistry under high pressures in the near future. [39-40]

## **IV) High Pressures in Biosciences**

The use of High Pressures in this domain is more and more developed. [41, 42]  
Pressure effects concern mainly :

- the weak chemical bonds,
- the structure of the proteins,
- the enzymatic reactions

and also some specific interactions as :

- protein-protein,
- protein-nucleic acid,
- protein-solvent.

The role of the solvation is important :

$$\Delta V_{\text{app.}} = \Delta V_{\text{chemistry}} + \Delta V_{\text{conformation}} + \Delta V_{\text{solvation}}$$

## Conclusions

Chemical bonding is a critical phenomena for inducing physico-chemical properties of materials.

The influence of high pressures conditions has been divided in two parts :

- (i) the modification of the chemical bond inducing mainly the modification of structural and/or electronic properties,
- (ii) the formation of chemical bonds through the synthesis of new materials.

High pressures appear to be a powerful tool for modifying or inducing chemical bonds and could be developed in the future for improving Solid State Chemistry and Materials Science.

## References

- (1) P. ADLER, U. SCHWARTZ, K. SYASSEN, G. Kh. ROZENBERG, G. Yu MACHAVARIANI, A.P. MILNER and M.P. PASTERNAK.  
*Physical Review B*, Vol. **60** (7) (1999), p. 4609.
- (2) M. TAKANO, S. NASU, T. ABE, K. YAMAMOTO, S. ENDO, Y. TAKEDA and J.B. GOODENOUGH.  
*Phys. Rev. Letters*, Vol. **67** (23) (1991), p. 3267.
- (3) C.P. SLICHTER and H.G. DRICKAMER.  
*J. Chem. Phys.*, Vol. **56** (5) (1972), p. 2142.
- (4) M.P. PASTERNAK, R.D. TAYLOR, M.B. KRUGER, R. JEANLOZ, J.P. ITIE and A. POLIAN.  
*Phys. Rev. Letters*, Vol. **72** (17), (1994), p. 2733.
- (5) J.F. LONGO and J.A. KAFALAS.  
*Mat. Res. Bull.*, Vol. **3** (1968), p. 687.
- (6) G. DEMAZEAU, F. MENIL, J. PORTIER and P. HAGENMULLER  
*C.R. Acad. Sc.*, Vol. **273** (1973), p. 1641.
- (7) C. DELMAS, G. DEVALETTE, M. DEVALETTE, C. FOUASSIER and P. HAGENMULLER.  
*J. Solid State Chem.*, Vol. **19** (1976), p. 87.
- (8) T. GRANDE, S. JACOB, J.R. HOLLOWAY, P.F. MAC MILLAN and C.A. ANGELL.  
*J. Non Cryst. Solids*, Vol. **184** (1995), p. 151.
- (9) J.J. CAPPONI, J. CHENAVAS and J.C. JOUBERT.  
*Bull. Soc. Mineral. Crystallogr.*, Vol. **95** (1972), p. 412.



- (10) B.L. CHAMBERLAND.  
*Mat. Res. Bull.*, Vol. **6** (1971), p. 311.
- (11) G. DEMAIZEAU, J. GRANNEC, A. MARBEUF, J. PORTIER and P. HAGENMULLER.  
*C.R. Acad. Sc.*, Vol. **269** (1969), p. 987.
- (12) G. DEMAIZEAU, D.Y. JUNG, A. LARGETEAU and J.H. CHOY.  
*The Review of High Pressures and Technology*, Vol. **7** (1998), p. 1025.
- (13) F. KANAMARU, H. MIYAMOTO, Y. MIMURA, M. KOIZUMI, M. SHIMADA, S. KUME and S. SHIN.  
*Mat. Res. Bull.*, Vol. **5** (1970), 257
- (14) Y. TAKEDA, S. NAKA, M. TAKANO, T. SHINJO, T. TAKADA and M. SHIMADA.  
*Mat. Res. Bull.*, Vol. **13** (1978), 61.
- (15) G. DEMAIZEAU, B. BUFFAT, F. MENIL, L. FOURNES, M. POUCHARD, J.M. DANCE, P. FABRITCHNYI and P. HAGENMULLER.  
*Mat. Res. Bull.*, Vol. **16** (1981), p. 1465.
- (16) G. DEMAIZEAU, M. POUCHARD and P. HAGENMULLER.  
*J. Solid State Chem.*, Vol. **9** (1974), p. 202.
- (17) B. BUFFAT, G. DEMAIZEAU, R. BLACK, Y. TAKEDA, M. POUCHARD and P. HAGENMULLER.  
*C.R. Acad. Sc.*, Vol. **295** (1982), p. 557.
- (18) G. DEMAIZEAU, A. MARBEUF, M. POUCHARD and P. HAGENMULLER.  
*J. Solid State Chem.*, Vol. **3** (1971), p. 582.
- (19) G. DEMAIZEAU, C. PARENT, M. POUCHARD and P. HAGENMULLER.  
*Mat. Res. Bull.*, Vol. **7** (1972), p. 913.
- (20) P. BERNIER and S. LEFRANT.  
**Le Carbone dans tous ses états**. Chapitre 13.  
G. DEMAIZEAU "Diamant et Matériaux Dérivés"  
*Gordon and Breach Science Publishers* (1997).
- (21) R.H. WENTORF Jr.  
*J. Chem. Phys.*, Vol. **26** (1957), p. 956.
- (22) A.R. BADZIAN.  
*Mat. Res. Bull.*, Vol. **16** (1981), p. 1385.
- (23) Y. FUJIKI and T. OIKAWA.  
*Chem. Mater.*, Vol. **5** (1993), p. 695.

- (24) H.T. HALL and L.A. COMPTON.  
*Inorg. Chem.*, Vol. **4** (1965), p. 1213.
- (25) T. ENDO, T. SATO and M. SHIMADA.  
*J. Mat. Sc. Lett.*, Vol. **6** (1987), p. 683.
- (26) A.Y. LIU and M.L. COHEN.  
*Science*, Vol. **245** (1989), p. 841.
- (27) R.C. de VRIES.  
*Mat. Res. Innovat.*, Vol. **1** (1997), p. 161.
- (28) S. MATSUMOTO, E.Q. XIE and F. IZUMI.  
*Diamond and Related Materials*, Vol. **8** (1999), p. 1175.
- (29) D.M. TETER and R.J. HEMLEY.  
*Science*, Vol. **271** (1996), p. 53.
- (30) H. MONTIGAUD, B. TANGUY, G. DEMAZEAU, I. ALVES and S. COURJAULT.  
*J. of Mat.*, Vol. **35** (2000), p. 2547.
- (31) A.W. SLEIGHT.  
*Inorg. Chem.*, Vol. **7** (9) (1968), p. 1704.
- (32) Th. PLANTE, G. DEMAZEAU, M. POUCHARD and P. HAGENMULLER.  
*Bull. Soc. Chim. Fr.*, Vol. **12** (1974), p. 202.
- (33) H. FUJINAKA, N. KINOMURA, Y. MIYAMOTO, S. KUME and M. KOIZUMI.  
*High Pressure Science and Technology*, Vol. **1** (1979), p. 556 - Pergamon Press.
- (34) A.W. SLEIGHT.  
*Inorg. Chem.*, Vol. **8** (8) (1969), p. 1967.
- (35) R.D. SHANNON and A.W. SLEIGHT.  
*Inorg. Chem.*, Vol. **7** (8) (1968), p. 1649.
- (36) R. ATOU, M. HASEGAWA, L.J. PARKER and J.V. BADDING.  
*J. Am. Chem. Soc.*, Vol. **118** (1996), p. 12104.
- (37) M. HASEGANA, T. ATOU and J.V. BADDING.  
*J. Solid State Chem.*, Vol. **130** (1997), p. 311.
- (38) J.S. TSE, G. FRAPPER, A. KER, R. ROUSSEAU and D.D. KLUG.  
*Physical. Rev. Lett.*, Vol. **82** (22) (1999), p. 4472.
- (39) G. DEMAZEAU.  
*J. Mater. Chem.*, Vol. **9** (1999), p. 15.
- (40) J.M. LONGO and J.A. KAFALAS.  
*Mat. Res. Bull.*, Vol. **3** (1968), p. 687.