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PROBLEMS OF SOLID STATE CHEMISTRY UNDER HIGH PRESSURE CONDITIONS : A PERSPECTIVE FOR ELABORATING NEW MATERIALS*

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Use of high pressures for preparing either classical materials with a high rection speed or novel materials is illustrated by appropriate examples involving in particular high oxidation states. The technique has also been applied to crystal growth or to phase transformations favoured by lattice shrinking. The importance of high pressure as a physical parameter in modern solid state chemistry is emphasized.

Key Words : Solid State Chemistry; Synthesis; Structural Transformations; High Pressure; High Oxidation States

INTRODUCTION

THE high pressure technique is quite an efficient tool for preparing new materials of weak stability or of metastable character in solid state chemistry.

During the last few years it has led to a growing number of contributions, especially in three areas :—

— Synthesis of new materials either for better basic approach of scientific problems or for industrial applications.

— Structural transformations.

— *In situ* evolution of some physical properties under increasing pressure.

SYNTHESIS OF NEW MATERIALS

The performances have developed much thanks to utilization of equipments allowing higher pressures with better reliability and more safety. Figs. 1 and 2 give examples of apparatus used either for solid-gas reactions or for solid state synthesis.

The most important features in high pressure synthesis are either of kinetical nature or a stabilizing effect.

Kinetical Aspect

The reactions in high pressure conditions are considerably accelerated as far the expected material becomes thermodynamically more stable under pressure.

Such a behaviour is clearly illustsated by the synthesis of the distorted perovskite $GdFeO_3$: at atmospheric pressure at about 1000 °C, 50 hours are necessary to prepare a pure perovskite phase from the stoichiometric mixture of the starting

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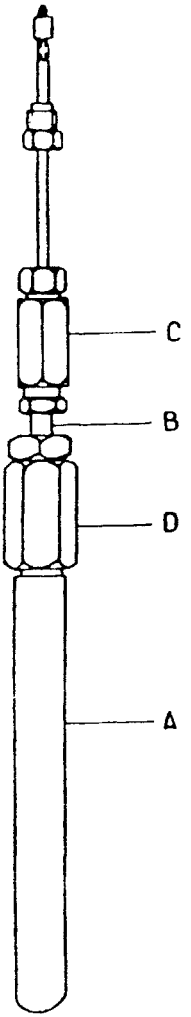
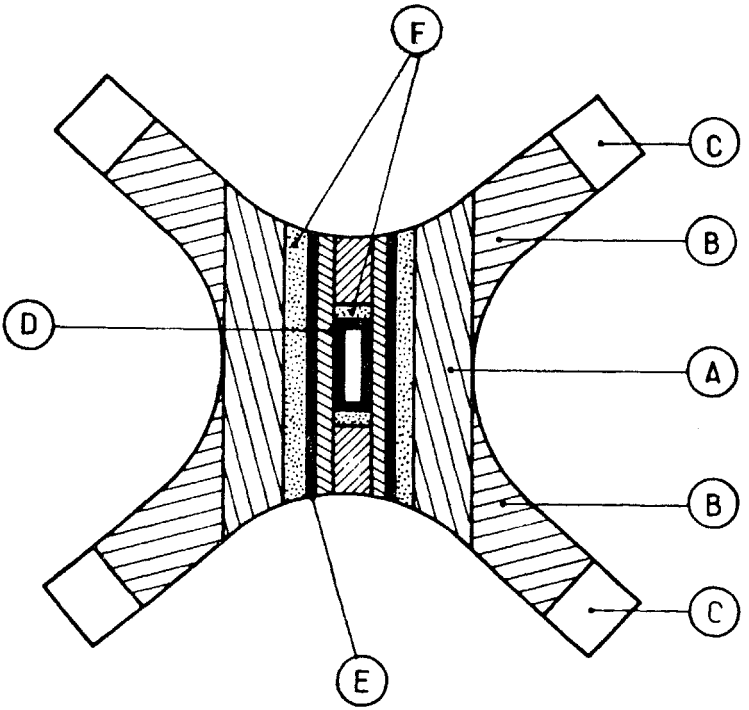


← FIG 1 Cold gasket gas reaction tube—A : reaction cylinder in refraction cylinder in refractory alloy, B : closing path, C : high pressure gasket, D : air proof crown.



↑ FIG 2 Belt-type apparatus used for reactions in sealed tubes (in solid state or of gas-solid type).

binary oxides. At the same temperature under 50kb pressure a much shorter time—between 8 and 10 minutes—is sufficient for realizing the same synthesis process.[1]

High Pressure and Thermal Decomposition

High pressures are also extremely suitable to prevent unstable starting oxides from thermal decomposition, when the reaction requires normally high temperatures. This stabilization effect can be illustrated by the synthesis of the mercury tungsten bronzes Hg_xWO_3. In spite of the thermal instability of HgO, Hg_xWO_3 bronzes have been elaborated under 3kb pressure.[2]

New lead (IV) compounds the preparation of which requires unstable lead dioxide such as the $La_2Pb_2O_7$ pyrochlore have been obtained in a similar way.[3]

High Pressure and Disproportionation

High pressure can hinder disproportionation and favour on contrary stabilization of intermediate states. Let us quote as an example chromium (IV) which is unstable in an octahedral site, disproportionating when heated at normal pressure into oxidation states III and VI : $3Cr(IV) \rightarrow 2Cr(III) + Cr(VI)$, as oxidation state III is favored in an O_h surrounding by $t_{2g}^3 e_g^0$ configuration and o.s. VI by strong covalency within the CrO_4 tetrahedron. Nevertheless, under oxygen pressure chromium dioxide can be prepared either by hydrothermal reduction[4] of CrO_3 or by oxidation[5] of Cr_2O_3. Due to its ferromagnetic properties CrO_2 is as acicular tiny particles a good magnetic taperecording material.[6]

High Pressure and Negative Variation of Unit Cell Volume

The preparation under pressure of rare earth monoxides has been investigated by Léger *et al.*[7]

The Gibbs free energy ΔG corresponding to the synthesis : $Ln + Ln_2O_3 \rightarrow 3LnO$ (Ln : rare earth) is positive at ordinary pressure for most rare earths, but negative for europium (this value explains why only EuO is stable in normal pressure conditions).

Under high pressure, resulting from a negative value of the unit cell volume ΔV ,a $P\Delta V$ term can compensate the initial positive value of ΔG as far pressure is high enough. Such a phenomenon favours the synthesis of new rare-earth monoxides, e.g. SmO between 15 and 60kb pressure.

High Pressure and Stabilization of Materials with Intermediate Properties

In preventing from certain lattice instabilities, high pressures are able to stabilize materials intermediate between those described by classical models.

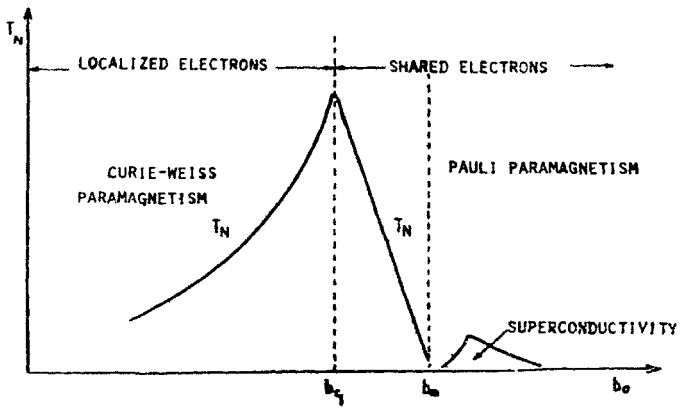


FIG 3 Plot of T_N against transfer integral b_σ for $n = 1(8)$.

Let us quote the $LnNiO_3$ perovskites prepared under high oxygen pressure with properties ranging between those of insulating and metallic metarials, a situation nature likes to by-pass in the absence of an appropriate driving force.

The localization of the e_g electron of low spin nickel (III) depends on the covalency of the (Ni—O) σ bond as already shown by Goodenough from its (b_σ, T_N) diagram (Fig. 3).

$LaNiO_3$ can already be prepared at atmospheric pressure with a small rhombohedral distortion.[8] Due to large size of La^{3+} the overlapping of the nickel(III) σ-orbitals with the p orbitals of oxygen is nearly forming a 180° angle ($b_\sigma > b_m$ in Goodenough's diagram) and $LaNiO_3$ is metallic with a Pauli type paramagnetism.

For the other $LnNiO_3$ perovskites high pressure is necessary to synthesize the stoichiometric oxides.[9] Due to smaller size of the rare earth the distortion of the unit cell increases and the Ni—O—Ni angle decreases from 180 °C, all the more as Ln^{3+} is shrinking. Weaker orbital overlapping leads to disappearing metallic character. The lower covalency of the $(Ni—O)_\sigma$ bonds accounts for the use of high pressures for the elaboration of the materials, which are no more thermodynamically stable under ordinary pressure. Table I illustrates the evolution of the Ni—O—Ni angles with the rare earth considered.[10]

TABLE I

Ni—O—Ni angles in the $LnNiO_3$ oxides of perovskite or perovskite derived $GdFeO_3$ structure (Ln : rare earth)

	Along z-axis	In the xy plane
$NdNiO_3$	159.1°	159.5°
$SmNiO_3$	152.8	153.5
$EuNiO_3$	149.7	150.3
$GdNiO_3$	147.4	148.5
$DyNiO_3$	145.2	147.2
$YNiO_3$	142.9	145.4
$ErNiO_3$	142.1	145.4
$TmNiO_3$	142.4	145.2
$YbNiO_3$	141.3	144.7
$LuNiO_3$	140.2	143.5

As shown in Fig. 4 the variation of reciprocal magnetic susceptibility vs temperature for $YNiO_8$ and $LuNiO_3$ (where the rare earths are diamagnetic) is consistent with a certain degree of electronic localization ($b_c < b_\sigma < b_m$). The slope is smaller nevertheless than that which would correspond to a perfect $t_{2g}^6 e_g^1$ localization ($b_\sigma < b_c$), a feature consistent with absence of a Jahn-Teller distortion in the lattice.

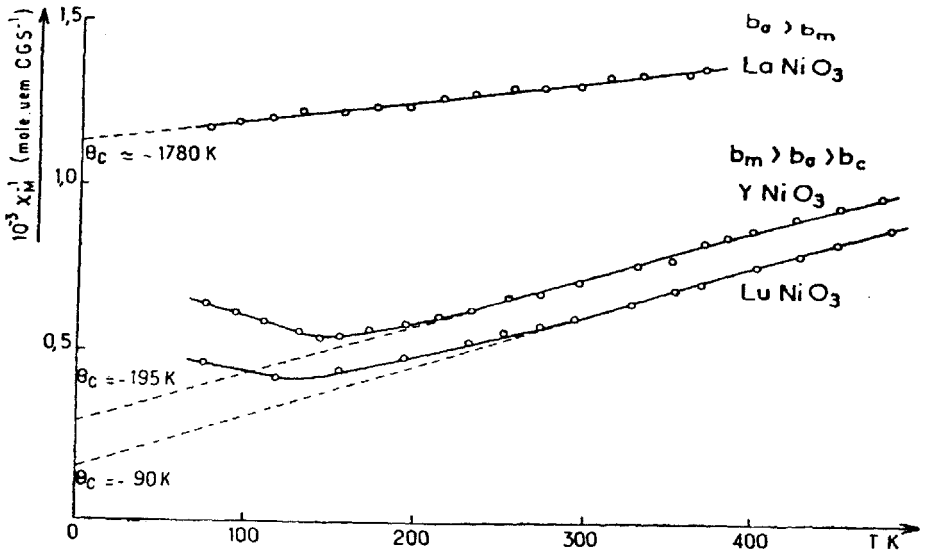


FIG 4 Variation of the reciprocal molar magnetic susceptibility *vs* temperature for the $YNiO_3$, $LaNiO_3$ and $LuNiO_3$ phases.

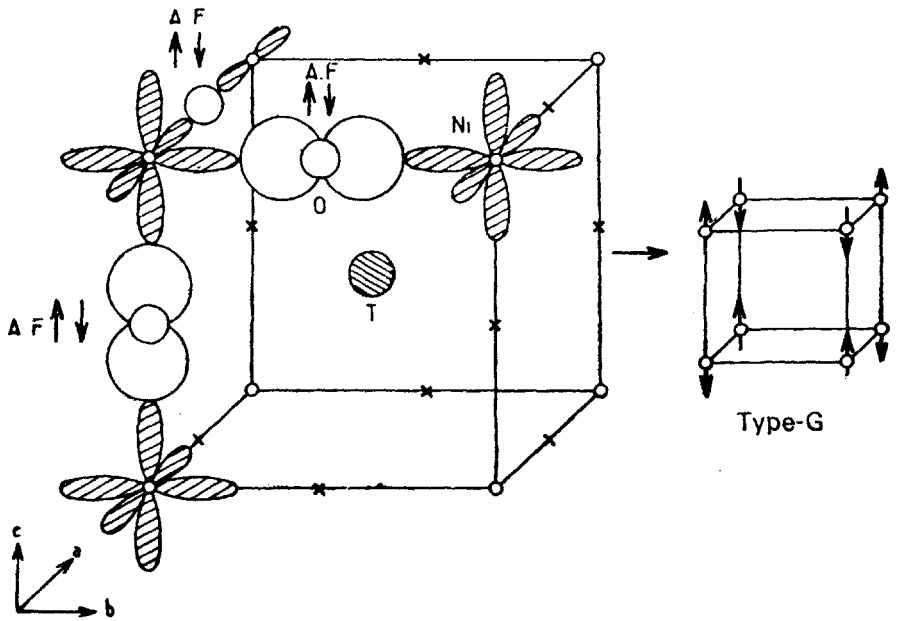


FIG 5 Suggested magnetic couplings for $YNiO_3$ and $LuNiO_3$.

In fact in $YNiO_3$ and $LuNiO_3$ a uniform distribution of the e_g electron around Ni^{3+} appears, but without real delocalization in the whole lattice like in $LaNiO_3$ (Fig. 5).

Attempts to synthesize at atmospheric pressure materials intermediate between insulators and Pauli paramagnetic behaviour lead mostly to disproportionation into two phases with respective insulating and metallic character.

High Pressure and Stabilization of High Oxidation States

The preparation of unusual oxidation states of transition elements depends on the posibility of stabilizing the corresponding electronic configurations.

Using sppropriate structural and chemical bonding factors, high oxygen pressure synthesis can lead to unusual high oxidation states.

This possibility is illustrated in a spectacular way by the stabilization of six-coordinated iron (V) which has been obtained recently for the fist time in an oxide. Fe(V) had only been reported so far in oxides as traces or in tetrahedral coordination.[11,12,13]

With a $t_{2g}^3 e_g^0$ electronic configuration in an octahedral site, iron (V) has an isotropic electronic distribution ($^4A_{2g}$ ground term). Such an electronic configuration may fit very well with a site of O_h symmetry. But the high ionization potential of iron (V) requires a covalency of the Fe—O bonds strong enough to stabilize the $t_{2g}^3 e_g^0$ configuration.

Synthesis of an oxide containing Iron (V) is only possible under high oxygen pressure. Therefore, we had to select a structure able to be very stable under such conditions. The most convenient one, having both high stability and an O_h symmetry site, appeared to be the perovskite structure.

To enhance the covalency of the Fe—O bond it was brought in competition with 6 weak Li—O bonds surrounding each FeO_6 octahedron (Fig. 6).

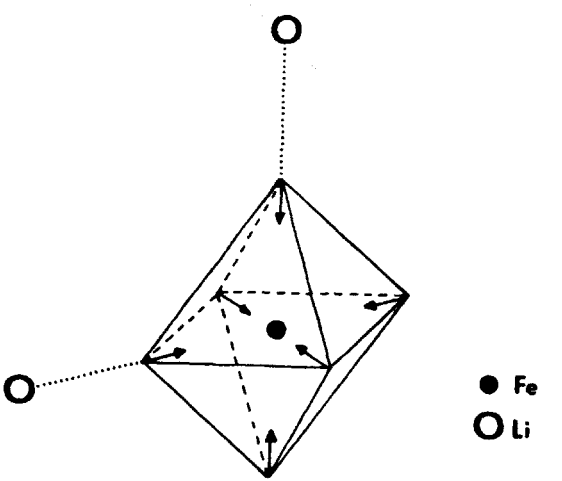


FIG. 6 Formation of a FeO_6 octahedron with iron (V) in La_2LiFeO_6.

According to this prediction the La_3LiFeO_6 phase has been recently prepared under high oxygen pressure (70kb). Lanthanum was selected by reasons of size and charge.[14] The thermal decomposition *in situ* of unstable $KClO_3$ was used as an oxygen source in the sealed reaction tube. After quenching KCl was quickly leached out with water.

The new material has been characterized chemically and physically, in particular by magnetic measurements (Fig. 7) and Mössbauer spectroscopy (Fig. 8).

If we compare the various chemical shifts observed by the latter technique for iron in various oxidation states, the strongly negative value obtained appears to characterize both oxidation state V and strong covalency of Fe—O bonding.

ESR measurements have also shown an excellent agreement between the observed g-value in La_2LiFeO_6 ($g \simeq 2.0135$) and the experimental one claimed

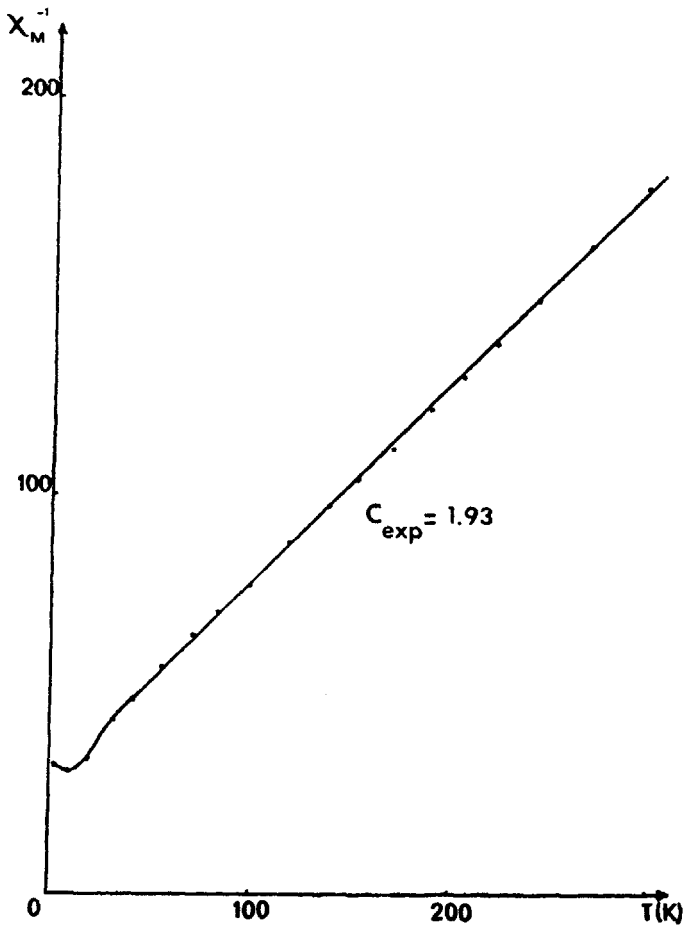


FIG 7 Reciprocal molar susceptibility of La_2LiFeO_6 *vs* temperature characterizing formation of Iron (V).

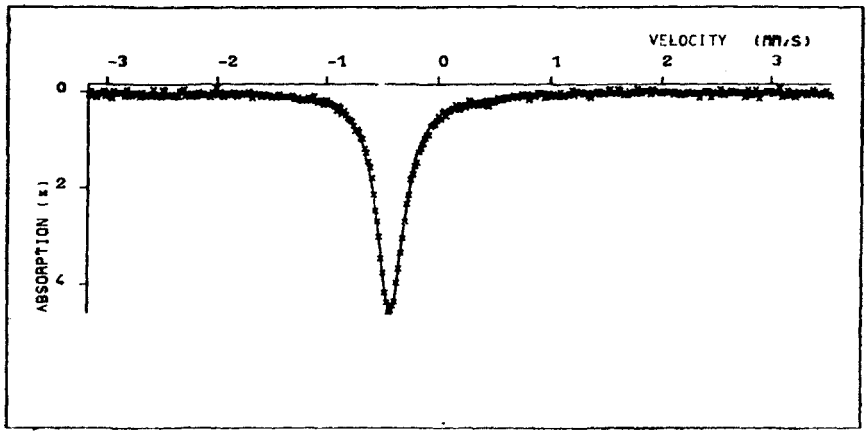


FIG 8 Mössbauer resonance spectrum of La_2LiFeO_6 at 293 K (*source* : ^{57}Co in a rhodium matrix).

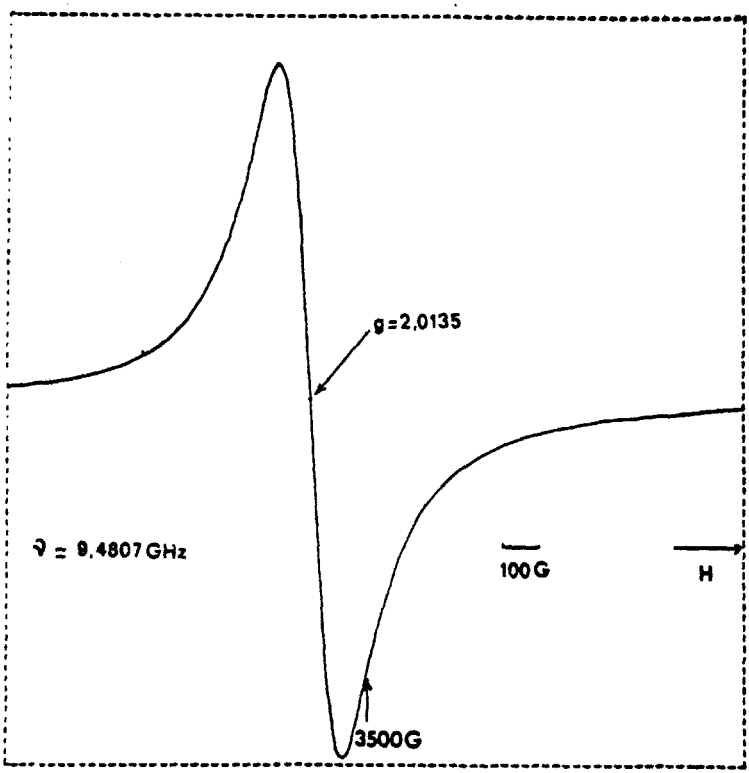


FIG 9 ESR spectrum of La_2LiFeO_6 at 293 K.

before by Müller *et al.* ($g \simeq 2.0131$) for $SrTiO_3$ containing traces of Fe(V) as substitutional defects[13] (Fig. 9).

Let us mention that homologous La_3LiRuO_6 and La_2LiOsO_6 perovskites have been prepared even at ordinary pressure thanks to higher crystal field of ruthenium (V) and osmium (V) which are respectively 4*d* and 5*d* ions.

Higa oxygen pressures are obviously the best way for stabilizing unusual high oxidation states of transition elements, in particular 3*d*-elements (e.g. Fe(IV), Fe(V), Co(IV), Ni(III), Cu(III). The most appropriate structures for obtaining given electronic configurations, for instance HS iron (IV) or LS nickel (III), can be predicted on hand of relatively simple models and effectively set up.[15]

High pressure fluorine leads in an analogous way to high oxidation state fluorides, e.g. Cs_2NiF_6, Cs_2CuF_6 or Cs_4GaAgF_{12}.[16]

High Pressure and Elaboration of Defect-Free Entities

The use of fluids in supercritical conditions under high pressure allows elaborating almost defect-free single crystals either for basic research or even for industrial applications. A similar technique can be used for preparing tiny grains as a first step in ceramic formation processes. Absence of differences in superficial tensions avoids formation of microcracks and enhances strongly the mechanical properties of the ceramics.

As an example large size high quality single crystals of quartz can be easily prepared at 400 °C under 1.5kb pressure using polycristalline quartz as starting material and an alkaline solution as transport fluid.[17]

Structural Transformations under Pressure

High pressure increases the density of the materials and as a consequence decreases the interatomic distances. Hence, the steric or electrostatic interactions are enhanced. The materials evolve so as to minimize such effects.

High pressure structural transformations are quite important in connection with explanation of geological processes as well as applications (e.g. the graphite→diamant or boron nitride→borazon transformations).

In first approximation two types of transitions may be observed :

(*A*) those without increase in coordination number

(*B*) those with increasing coordination.

Without Increasing CN

The first transformation type can be illustrated by some significant examples :

— Structural transformation of the hexagonal perovskites.

— Structural transformation of the Li_2MF_6 fluorides.

For the perovskites, the structural distortion depends closely on the Goldschmidt structural factor *t*. For $t = 1$ cubic symmetry is observed. When $t > 1$ hexagonal or rhombohedral varieties appear. For the largest *t*-values all layers have a hc type-packing, all BX_6 octahedra share faces with each other to form chains parallel to the *c*-axis (2H structure).

On the other hand, if the packing is of *cfc*-type, the octahedra form a three dimensional network sharing only corners and resulting in the well-known cubic perovskite structure ($t = 1$).

For intermediate t-values stackings having alternately hc and *cfc*-packed layers can exist (Fig. 10).

Under pressure, owing to the short cationic distances across the common faces of the octahedra and hence to strong electrostatic repulsion between the concerned *B* cations, an evolution from face sharing to corner sharing octahedra is observed : the number of blocks with face sharing octahedra decreases in the lattice : 2H → 9H → 4H → 6H → 3C structural transformations can be observed.[18]

Some of the intermediate phases may show ferromagnetic behavior as far appropriate magnetic cations occupy two different sites (for instance in 6H-type $RbFeF_3$).

Many other examples illustrate transformations without change of the coordination number, but with reduced cationic repulsion due to structural shifts :

e.g. $A^{VI}B^{VI}O_4$ (rutile) → $A^{VI}B^{VI}O_4$ (α—PbO_2)

For the Li_2MF_6 fluorides[19] three structural types occur and the transformation from each other results from a modification of the positions of the cations in the *hc* lattice of the fluoride ions. The increase in the size of the M^{4+} ion as well as increasing pressure leads to stronger electrostatic repulsion. As a consequence decrease in the number of edges shared by the (MF_6) and (LiF_6) octahedra is observed.

As illustrated by Fig. 11 transformations type I → type II → type III may be successively observed according to this rule. The number of common edges is successively 3, 2 and 0.

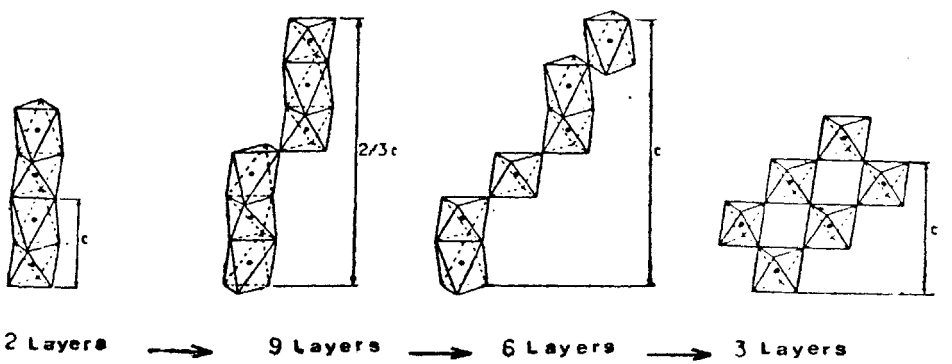


FIG 10 Structural evolution *vs* pressure for some ABX_3 polytypes—Increasing pressure gives rise to shift from left to right.

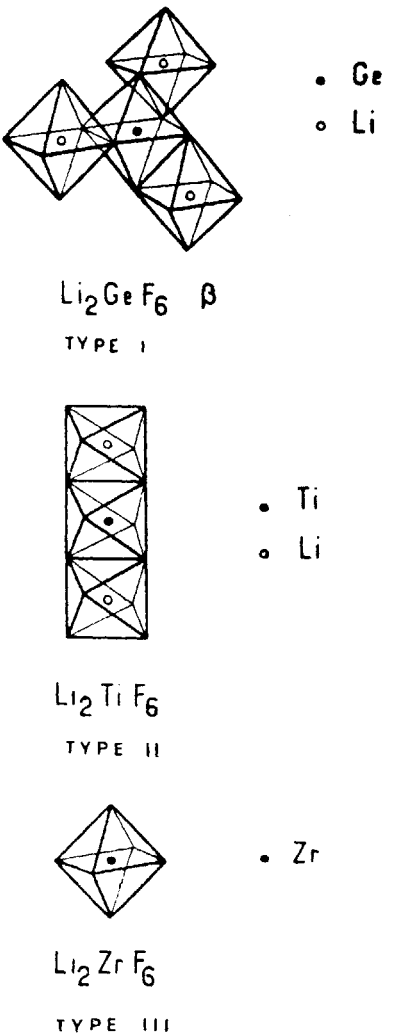


FIG 11 Structural evolution *vs* pressure for the Li_2MF_6 fluorides (from type I to type III).

With Increasing CN

The examples of transformations under high pressure with increase in CN are numerous. Higher coordination increases the compactness of the lattice and is indeed favoured by pressure.

The phase transition recently observed for PdF_2 under pressure is a good illustration of this phenomenon. A large number of compounds with MX_2 general formulation derive from three main structural types : quartz, ratile and fluorite. They are characterized by the respective coordination number of cations and anions :

IV-II for quartz-type

VI-III for rutile-type

VIII-IV for fluorite-type.

Concerning the *d* elements, if we consider the whole set of so far known MX_2 oxides and fluorides only ZrO_2 and HfO_2 show at atmospheric pressure a structure derived from the fluorite-type.

The comparative stability of the rutile and fluorite-type structures depends primarily on the ratio of the cation/anion radii. For relatively small values of this ratio MX_2 compounds cristallize with the rutile structure and for the largest ones the stable form observed should be the fluorite-type. It is almost the case for the ZrO_2 and HfO_2 oxides, of baddeleyite type at low temperature (a structure actually close to that of CaF_2) and of fluorite-type at high temperature.

Among the *d* element difluorides PdF_2 with rutile structure shows the highest $r_{M^{2+}}/r_{F^-}$ ratio and appears to be the most favorable compound to be investigated under high pressure conditions.

Tressaud *et al*[20] ratio have recently obtained a cubic high pressure form of PdF_2, quenchable to room conditions.[19] The anionic environment of palladium 2 + derives from that of the fluorite-type by a rhombohedral distortion of the fluorine cubes (Fig. 12).

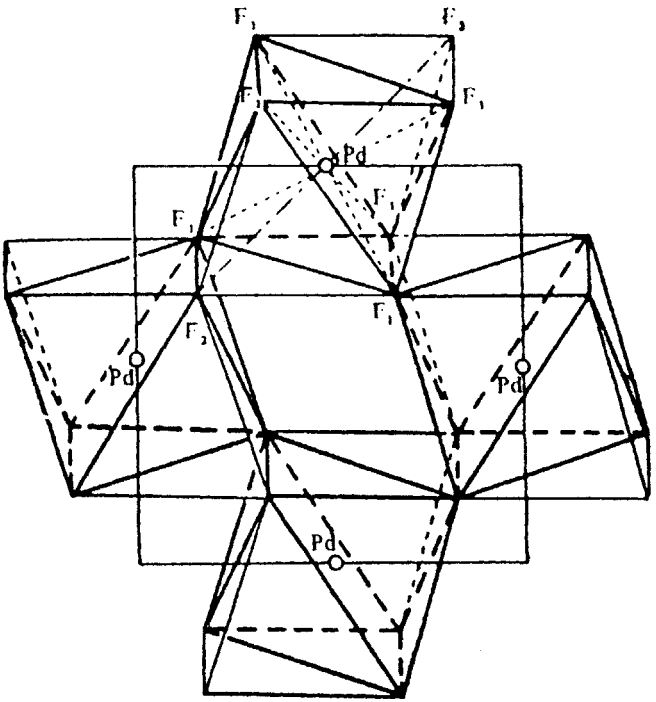


FIG 12 Structure of H.P. PdF_2 : projection on a (001) plane of the anionic environment of Pd atoms at $z = 0.5$.

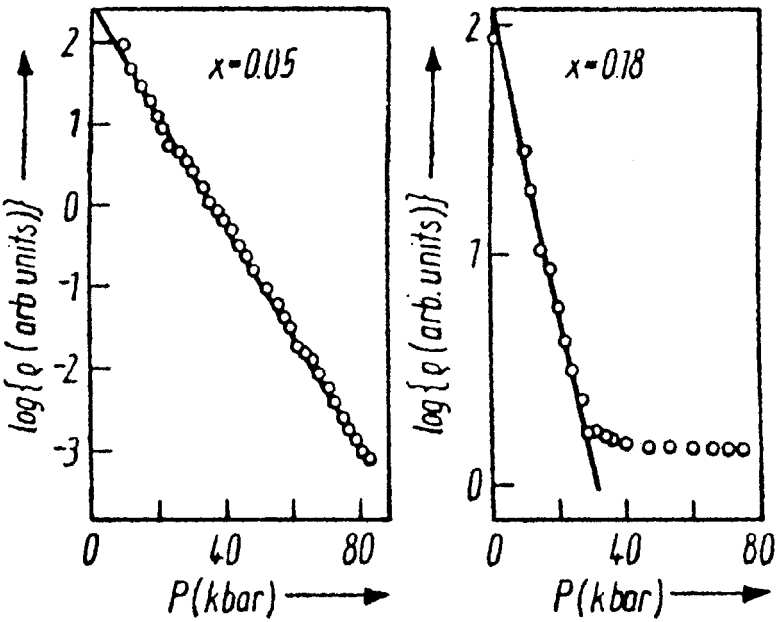


FIG 13 Variation of the logarithm of the resistivity with pressure at room temperature for $Eu^{2+}_{1-x}\,Nd^{3+}_{x}\,N_xO_{1-x}$ ($x = 0.05$ and $x = 0.18$).

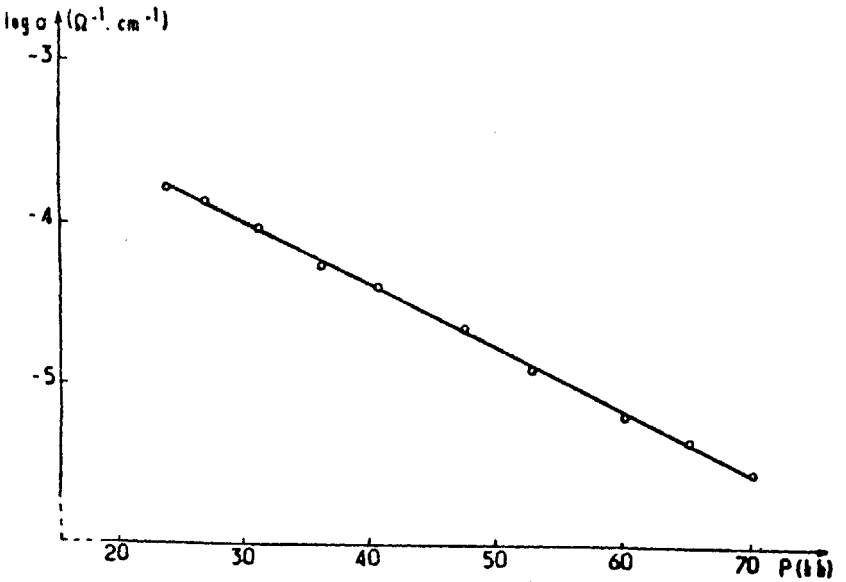


FIG 14 Variation of the logarithm of the conductivity with pressure at 300 K for $PbSnF_4$.

Evolution of Some Physical Properties Under Pressure

Many physical properties have been investigated under high pressure conditions, e.g.:

— electronic conductivity

— ionic conductivity

— ferroelectric behaviour.

They are all very sensitive to the cation-cation or anion-anion distances.

The most famous result is the metallic behavior of solid hydrogen under very high pressure claimed by Vereshagin.[21]

For EuO the promotion of a $4f$ electron into a $5d$ state due to broadening of the $5d$ band occurs at 300kb, leading to a non metal ⇒ metal transition.[23] The same phenomenon has been observed recently at lower pressure for rare earth oxynitrides $Eu^{2+}_{1-x}Ln^{3+}_{x}N_xO_{1-x}$.[23] The introduction of $4f$ electrons into the $5d$ type-conduction band is all the more easy as x is higher due to stronger covalency and $5d$ band broadening (Fig. 13).

For mobile ions in superionic conductors shrinking of the opening windows in the structural pathways with increasing pressure induces for most materials reduced ionic conductivity. Such a phenomenon has been observed recently for $PbSnF_4$, the best so far known anionic conductor[24] (Fig. 14).

Conclusion

High pressure technique appears to be quite an efficient tool in solid state chemistry, not only for new fundamental investigations (new elaboration methods, structural transitions, semiconductor-metal transitions), but also in the development of novel materials or in the improvement of worthwhile properties. Owing to the fact that 90 per cent of the materials in the earth exist under pressures much higher than 100kb, high pressure is obviously also an important crossroad between different scientific areas and a factor of human progress.

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