The "supercompressed" state of matter as an investigation object in high-pressure chemistry

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The prospects of a new line of research in high-pressure chemistry are discussed, which is associated with investigations of chemical reactions accompanied by large volume effects at ambient pressure and, hence, resulting in greater compressibilities of the reaction products. The compounds formed by intercalation of alkali metals in graphite and intermetallic compounds formed between alkali metals and silver or Group V metals (Sb, Bi), which crystallize with the BiF_3 structural type, are considered as examples of "chemical compression."

Key words: high pressure, degree of compression, chemical compression.

The use of high pressure is one of the most efficient methods for inducing large changes in crystal structure, physical properties, and chemical reactivity.

Experimental studies of compounds under high-pressure conditions started in the 1930s and were related to the publication of classical studies by Bridgeman and his school. These studies were carried out using the Bridgeman setup, which operates according to the principle that states that the pressure experienced by a sample loaded between the tops of truncated cones multiplies the pressure applied to the bases of the cones. This multiplication factor is equal to the ratio of the bases area to the area of the so-called "anvil." In order to exert a 100-kbar pressure on a sample under an "anvil" with an area of ~1 mm^2, the load on a cone base with an area of 1 cm^2 should be 1 ton.

The development of setups using the pressure "multiplication" principle initiated a new stage in solid-state physics and helped to solve a number of important technological problems, for example, to synthesize artificial diamonds. Modern setups with diamond anvils permit successful investigation of the structure and physical properties of thin films existing under pressures of hundreds of kbar. Exceptionally high pressures, close to 1.5—2.0 Mbar, were attained in a study[1] of hydrogen "metallization." Unfortunately, this procedure allows working only with samples having very small weights.

Therefore, in studies of the reactivity and the mechanisms of chemical reactions at high pressures *in situ*, the processes occurring in a substance at the instant of compression can be judged in most cases only based on indirect data, in particular, on the composition and physicochemical characteristics of the final reaction products, stable after the high pressure has been released.

As a rule, these products are not identical to the matter formed upon compression. The information obtained in this way often helps in solving applied problems but is of little use for understanding the nature of chemical reactions under high and extremely high pressures. As an illustration, it can be noted that the mechanism of the processes involved in the industrial manufacture of the high-density cubic modifications of carbon and boron nitride, which occur even at relatively low (below 50 kbar) pressures, still remains unknown.

What happens to the substance under high-pressure conditions or, in other words, upon compression?

The "macroscopic," *i.e.*, the directly recordable, effect is associated with a decrease in the volume of the sample being compressed. Let V_0 and V be the atomic or molar volume of an element or compound at ambient pressure and at high static pressure P, respectively. Then volume effects, absolute ($\Delta V = V_0 - V$) and relative ($\Delta V/V_0$), and the degree of compression V/V_0 can serve as measures for the efficiency of this action. A parameter that can be used for individual compounds is compressibility $1/V(\partial V/\partial P)_T$, which can be determined experimentally by measuring the value $(\Delta V/\Delta P) \cdot 1/V$ (ΔP is the pressure range in which the pressure dependence of the volume is measured).

It is clear that the compressibility of a substance is directly related to the volume effects of the polymorphic transformations that can occur in the pressure range considered. When that transformation proceeds and especially when large volume effects are involved, the integral compressibility of the substance ($\sum \Delta V/\Delta P$), *i.e.*, the overall compressibility in this pressure range, is relatively high.

If the object of study is a mixture of substances prone to chemical interaction initiated by compression, the ΔV and $\Delta V/V_0$ values measured directly during the experiment can be regarded as the volume effects of this chemical reaction.

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The volume effect of a reaction $\Delta V/V_0$ is an independent macroscopic measure of the change of the structure and properties of a substance during a chemical reaction or a polymorphic transformation; it is as independent as the heat of the reaction or the change in the Gibbs free energy.

However, the "microscopic" effect, associated with the substantial changes in the configurations of the outer (valence) electron orbitals, is more important for the understanding of specific features of a chemical reaction under high-pressure conditions. An increase in the degree of compression is accompanied by an increase in the occupancy of the AO with large angular moments. In some substances possessing high compressibility, this change in the occupancy of electron levels occurs at relatively low pressures, while in other substances (with low compressibility), this occurs at pressures exceeding hundreds of thousands or millions of atmospheres.

For individual solid phases, the change in the occupancy of electron levels of atoms is accompanied by a change in the band structure and accounts for the baric polymorphim, which is observed, for instance, for cesium metal, possessing a very high compressibility at relatively low pressures.

Figure 1 shows the state diagram of cesium in the pressure range up to 60 kbar,[2] and Fig. 2 displays the degree of compression of cesium (V/V_0) and the occupancy of the 6s, 6p, and 5d AO[3] as functions of pressure using the previously reported data.[4,5] At pressures of ~50 kbar, the crystalline modification Cs^{IV} has a compression degree $V/V_0 \approx 0.4$ and a volume effect $\Delta V/V_0$ close to 60%. In this modification, cesium actually loses the properties of an alkali s-metal, because the occupancies of the 6s and 5d AO become virtually equal. The coordination polyhedron of the Cs atom in the Cs^{IV} modification is anisotropic and represents a combination of a square and a tetrahedron with Cs—Cs interatomic distances being equal[3] to 3.35 and 3.58 Å. The volume effect $\Delta V/V_0$ = 73% accompanies the transformation of cesium into the Cs^{V} modification, in which the occupancy of the 5d AO reaches 80%. The volume effect observed on passing to Cs^{VI}, which crystallizes at 720 kbar forming a hexagonal closest packing, similarly to "true" transition metals, amounts to 84%.

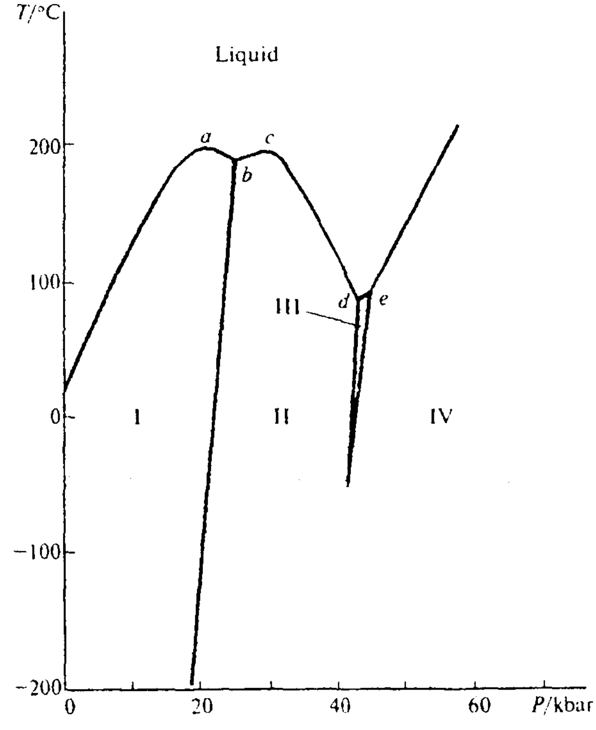

Fig. 1. State diagram of cesium: (*a*) 20.1 kbar, 200 °C; (*b*) 25.0 kbar, 191 °C; (*c*) 30.0 kbar, 198 °C; (*d*) 42.5 kbar, 88 °C; (*e*) 43.9 kbar, 98 °C.

Similar state diagrams have been constructed for rubidium and potassium; however, the phase transitions in these systems occur at higher pressures; in particular, potassium undergoes these changes at pressures above 100 kbar. In practice, this means that the occupancy of the 4d AO of a K atom at near ambient pressures is very low, which largely determines the chemical properties of this element in the "supercompressed" state.

Baric polymorphism, associated with an inversion of valence levels (in this particular case, 5d and 4f), is also known[6] for lanthanides, for instance, for Ce, Y and Ce alloys, *etc.*

Since the chemical properties of matter in the crystalline phase are determined by the structure of its valence band, which, in turn, depends on the configuration of the valence AO, a "supercompressed" substance occurs in a special state, which differs from its state under standard thermodynamic conditions "normal" for the Earth surface.

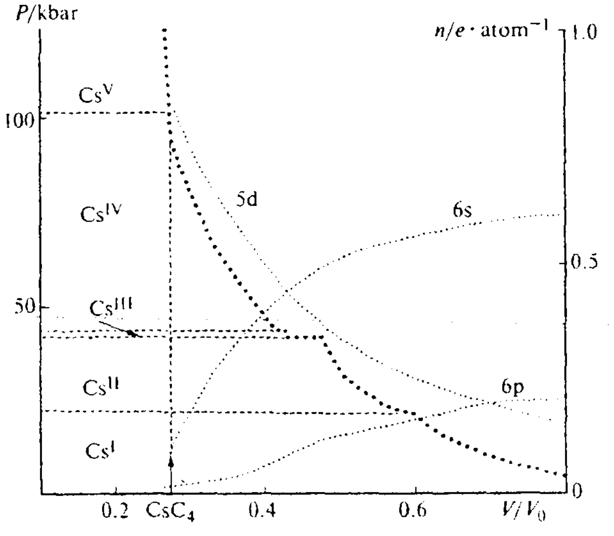

Fig. 2. Degree of compression V/V_0 at ~100 kbar and the occupancy of the 6s, 5d, and 6p AO (*n*) in crystalline cesium *vs* pressure. The arrow marks the degree of compression of Cs in C$_4$Cs, close to that in Cs^{V}.

Specifically, the state of matter is determined by the degree of its compression rather than by the external pressure.

Thus, alkali metal halides, due to their low compressibility, retain all the properties of ionic crystals even at very high pressures, reaching hundreds of kbar. The ionic type of bond and the physical properties of these compounds remain unchanged.

However, some typical nonmetals such as phosphorus, iodine, arsenic, and selenium, whose compressibility is much higher, show changes fundamental in their chemical behavior, acquiring properties of metals at lower pressures but at higher compression degrees.

It is significant for high-pressure chemistry that the "supercompressed" state of a substance does not necessarily arise when the substance is subjected to very high pressures.

Currently, a new approach to the study of substances at high compression degrees can be proposed; according to this approach, chemical reactions characterized by relatively low activation barriers but great volume effects at relatively low pressures become the main investigation objects.

In this case, the external pressure acts as a catalyst, which helps to reach the activation barrier by transforming the substance into the "supercompressed" state (Fig. 3).

This approach, referred to as the "chemical compression" principle,[7] does not necessitate the use of advanced high-pressure equipment and minute amounts of substances.

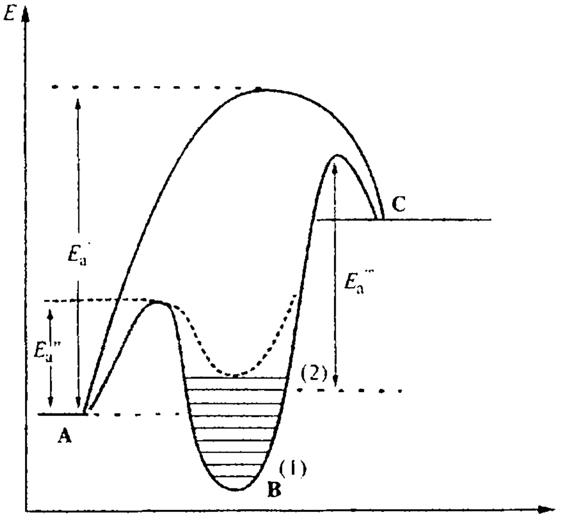

Fig. 3. "Supercompressed" state as a result of a chemical compression reaction. **A** is the initial state of the substance, **B** is the "supercompressed" state arising upon chemical compression, either thermodynamically stable (*1*) or metastable (*2*), **C** is the "supercompressed" state arising upon action of external high pressure; E_a', E_a'', and E_a''' are the activation energies of the corresponding reaction routes.

The "chemical compression" method differs fundamentally from the classical high-pressure methods in that it allows one to produce and study a "supercompressed" substance ($\Delta V/V_0 \geq 40\%$) at ambient pressures and in amounts (10^{-1}—10^2 g) sufficient for the reactivity of a "supercompressed" substance to be studied *in situ*.

Let us consider several examples illustrating the potentialities of this new approach.

The incorporation of alkali metals into graphite at atmospheric pressure is known to occur with low activation energies even on mere contact of the components. The intercalated compounds C_nM are distinguished by low heats and very large volume effects of formation.[8]

Intercalated compound	C_6Li	C_8K	C_8Rb	C_8Cs
$-\Delta V/V_0$ (%)	21.6	23.2	26.65	32.9

The atomic structure of graphite-like networks in compounds of this type remains virtually unchanged, and the deviations of the C—C interatomic distances in the regular C_6 hexagons do not exceed ±0.005 Å. These volume effects can be explained by "compression" of alkali metal atoms, which retain their high chemical reactivity toward electron acceptors.

It was suggested that under high pressures, it would be possible to obtain compounds formed by intercalation of alkali metals into graphite with higher contents and,

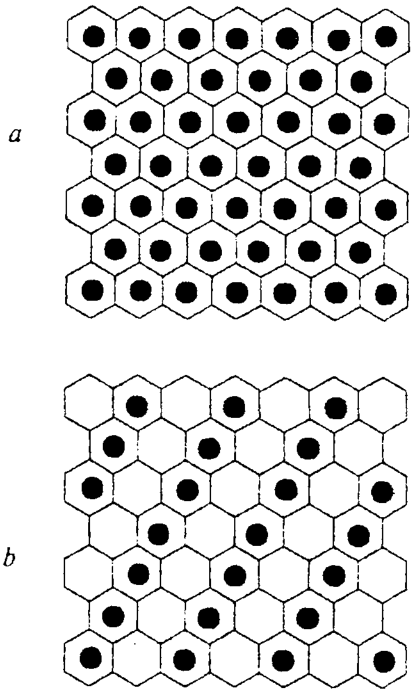

Fig. 4. Structure of the layers consisting of "supercompressed" metal atoms in C_2Li (*a*) and C_4Cs (*b*), metastable under atmospheric pressure

correspondingly, with higher degrees of compression of alkali metal atoms between the graphite-like layers. Experimental data confirming this hypothesis were obtained[9]; chemical compounds of the new type containing alkali metals in graphite and fullerene matrices were studied in detail.[4] It was found that at pressures not higher than 5—15 kbar, Li, K, Rb, and Cs form intercalated compounds with graphite with very high contents of alkali metal between the graphite-like layers composed of carbon atoms. The volume effects of formation of these compounds are very high.

Intercalated compound	C_2Li	C_4K	C_4Rb	C_4Cs
$-\Delta V/V_0$ (%)	42.6	40.1	44.9	48.2

The compounds C_2Li and C_4Cs, which are metastable at pressures close to atmospheric pressure, present special interest. Figure 4 shows the structure of layers formed by "supercompressed" atoms, established using X-ray diffraction,[10] IR, and NMR[11] data.

The layers of "supercompressed" Li atoms in C_2Li can be treated as planar infinite clusters, in which each Li atom is surrounded by six neighboring atoms, and the Li—Li interatomic distance is 2.46 Å. Two hexagons formed by C atoms are located at a distance of 1.86 Å from each Li atom.

In the structures of C_4Cs and, apparently, C_4K and C_4Rb, the clusters of "supercompressed" atoms of heavy alkali metals are linear; the M—M interatomic distances (2.46 Å) are much shorter than the M—M bond lengths (d) in the high-pressure modifications.

Phase	C_4Cs	Cs^{IV}	Cs^{V}
P/kbar	5—10	>45	>100
d(M—M)/Å	2.46	3.35—3.54	3.25—3.08

This interpretation of the nature of the chemical bond between the alkali metal and the graphite networks can be illustrated by the diagram of the electron levels shown in Fig. 5. Apparently, when Cs atoms are intercalated in graphite, the 5d AO of Cs, which is slightly occupied (see Fig. 2) at low pressures, interacts with the π-band of graphite to give a system of MO in which the bonding orbital(s) are located lower than the 6s AO level of the Cs atom. As a consequence, it is energetically more favorable for the valence electrons of Cs to pass into a new state, which is characterized by a large contribution of the low-symmetry 5d AO, having a large angular moment. This process of transformation of an alkali metal into the "supercompressed" state becomes more probable as the occupancy of the d AO in the free alkali metal at atmospheric pressure increases. This is in good agreement with the fact that the stability of compounds of the type C_4M decreases in the sequence C_4Cs > C_4Rb > C_4K. The K atom has the widest energy "gap" between the ns AO and the $(n-1)$d AO; therefore, C_4K can hardly exist at atmospheric pressure.[12] The Rb compounds occupy an intermediate position between the Cs and K compounds. The same regularity can be followed in the state diagrams of heavy alkali metals.

Apparently, the diagram of electron levels for C_2Li is similar, but in this case, the role of low-symmetry vacant or slightly occupied AO in the free metal is played by the Li 2p AO, located close to the 2s AO and important for the formation of tetrameric organolithium compounds.[13,14] Unlike Li and heavy alkali metals, sodium does not have low-symmetry AO located near valence 3s AO. This may account for the fact that no "supercompressed" state of alkali metal is formed on the interaction of sodium with graphite.

Another class of chemical compounds that can be taken as an example to consider the "chemical compression" principle is the class of intermetallic compounds M_nE. In these compounds, M is an alkali metal and E are Group IB—VB heavy metals (Au, Hg, Tl, Pb, Bi), more rarely, Ag and Cd, and also Sb, Sn, and Te. A common feature of these metals is the d^{10}-configuration and, correspondingly, the presence of a vacant f AO in the penultimate electron level adjacent to the valence level.

Table 1 presents the volume effects that accompany the formation of some compounds of the M_nE type at atmospheric pressure and for compounds K_2Ag and K_3Ag, prepared under high-pressure conditions.[15]

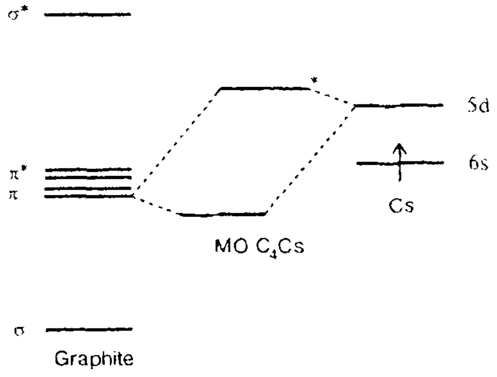

Fig. 5. Interaction of the electron levels of Cs and graphite accompanying the formation of the metastable C_4Cs.

Table 1. Volume effects ($-\Delta V/V_0$) of the formation of compounds in M—E systems

Compound	$-\Delta V/V_0$ (%)	P /bar	Compound	$-\Delta V/V_0$ (%)	P /bar
K_2Ag	62.5	$65 \cdot 10^3$	Cs_3Sb	45.1	1
K_3Ag	50.5	$65 \cdot 10^3$	Cs_3Bi	47.5	1
K_3Sb	35.2	$5 \cdot 10^3$	CsHg	30.5	1
K_3Bi	34.7	1	K_2Sn_3	34.3	1
Rb_3Sb	38.8	1	Cs_2Sn_3	38.0	1
Rb_3Bi	42.3	1			

The intermetallic compound K_2Ag is a structural analog of the graphite intercalated compound C_2Li. The structure of K_2Ag is formed by a network consisting of regular hexagons with vertices occupied by "supercompressed" K atoms. The positions corresponding to the Li atoms between the layers are occupied by Ag atoms. The K—K interatomic distances in the hexagons and the K—Ag distances in the AgK_6 pyramid are 3.13 and 3.628 Å, respectively. Since the atomic radius of K at 60 kbar is close to 1.90 Å, the decrease in the effective radius to 1.565 Å can be explained by "chemical compression" upon the formation of the graphite-like network involving 3d AO of K atoms, whose occupancy at 60 kbar differs from zero. Participation of the 4d AO of Ag atoms also cannot be ruled out, although the atomic radius of Ag in the crystal structure of K_2Ag is larger than the standard value by 0.63 Å.

Let us consider the structures of cubic phases of the composition M_3Bi (M is Li, K, Rb, or Cs), which crystallize according to the BiF_3 structural type. Cesium antimonide Cs_3Sb, lithium antimonide β-Li_3Sb, and K_3Ag belong to the same structural type.

All these compounds, except for K_3Ag and K_3Sb, can be prepared by simply fusing the elements together under atmospheric pressure. They possess metallic conductivity and luster and high chemical reactivity toward atmospheric oxygen and moisture, comparable to those of free alkali metals and quite unusual for compounds with ionic bonds. High chemical reactivity is also typical of β-Li_3Sb, synthesized by the reaction of antimony with a solution of lithium in liquid ammonia.

Compounds M_3E including K_3Bi have been synthesized and studied by X-ray diffraction analysis.[14–16] Sodium antimonide and bismuthide, whose formation is accompanied by smaller volume effects, crystallize with the Na_3As structural type, which differs from BiF_3.

A crystal structure of the BiF_3 type can be built of body-centered "cubes" with vertices occupied by alkali metal atoms M′ and centers occupied by alkali metal atoms M″ alternating with Sb, Bi, or Ag atoms (Fig. 6).

Let us assume that atoms located in the {0, 0, 0} and {1/2, 1/2, 1/2} positions in the "cubes" of the first and the second types "touch" each other, that the atomic volumes of M′ and M″ in the first type cubes are equal, and the atomic volumes of M′ in the first and second type cubes are identical. Then one can calculate the effective atomic radii of alkali metals, antimony, and bismuth in the "supercompressed" state under atmospheric pressure and those of potassium and silver at 65 kbar (Table 2).

These data indicate that the state of the alkali metal in the compounds M_3E differs substantially from the state of the M^+ ion; in lithium antimonide, and bismuthide, it can even be characterized as being close to the "covalent" state or a valence state with electrons collectivized in the metallic bond fashion. Heavy alkali metals in cesium antimonide and in cesium and rubidium bismuthides undergo noticeable compression. In particular, an atomic radius of cesium close to 2 Å corresponds to the degree of compression of cesium metal occurring in the Cs^{III} modification in which the s-electron has migrated almost completely to the low-symmetry 5d AO.[4,5]

In β-Li_3Sb and Li_3Bi, both the alkali metal atoms and Sb and Bi undergo "compression"; the Bi atom in Li_3Bi is "compressed" quite substantially. The atomic radius of Bi in Li_3Bi under atmospheric pressure (1.54 Å) is smaller than the atomic radius in the Bi^{VI} modification at 60 kbar (1.64 Å). Since sodium and potassium bismuthides and antimonides form no cubic phases with the BiF_3 structure under atmospheric pressure, it can be assumed that formation of the structure of

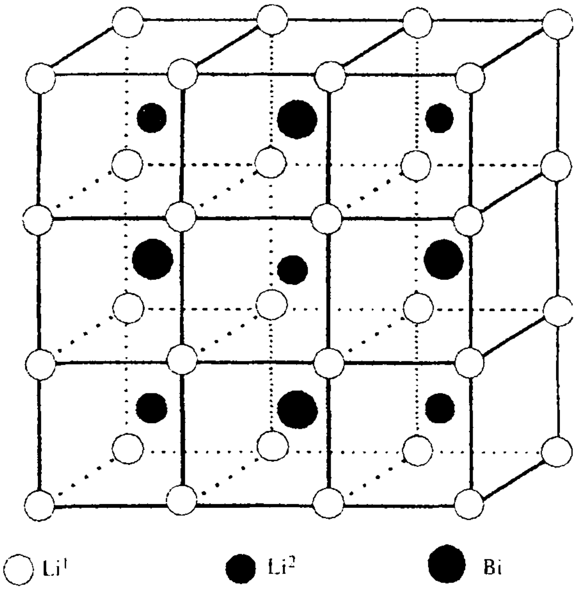

Fig. 6. Crystal structures of alkali metal pnictides. The BiF_3 structural type.

Table 2. Effective and standard atomic radii (Å) in M_3E

Compound	a_0[a]	d_{M-E}	R_{eff}[b]	R_M^0[c]	R_{M^+}[d]	R_E^0[e]
β-Li_3Sb	3.321	2.870	1.435	1.54	0.60	1.45
Cs_3Sb	4.592	3.976	1.988	2.66	1.69	1.45
Li_3Bi	3.354	2.905	1.452	1.54	0.60	1.77
K_3Bi	4.402	3.807	1.903	2.35	1.33	1.77
Rb_3Bi	4.495	3.893	1.946	2.52	1.48	1.77
Cs_3Bi	4.655	4.032	2.016	2.66	1.69	1.77
K_3Ag	3.918	3.395	1.903	2.35	1.33	1.44

[a] Size of the "cube" of M atoms.
[b] Effective radius.
[c] R_M^0 is the standard atomic radius.
[d] R_{M^+} is the ionic radius of the alkali metal cation.
[e] R_E^0 is the standard radius of the element.

the M_3E type is enabled by the possibility of the formation of an MO or a common valence band, arising upon interaction of the low-symmetry AO of Sb or Bi with the Li 3p AO or K, Rb, or Cs (n − 1)d AO, which are little occupied at ambient pressure. The energy level of this MO or "band" is lower than the level of the alkali metal s AO, occupied under atmospheric pressure. As a consequence, the formation of the M_3E cubic phase by lithium compounds is accompanied by a simultaneous decrease in the atomic volumes of M and E (see Table 2). In the case of compounds of heavy alkali metals, a relatively small increase in the atomic volume of element E is combined with a substantial compression of the alkali metal atom. A similar change is also observed upon the formation of "quasi-anions" based on $Sb^{\delta-}$ or $Bi^{\delta-}$ atoms and $Ag^{\delta-}$ "quasi-anions" in the isostructural compound K_3Ag, in which the atomic radius of Ag at 65 kbar is greater than the radius of metallic silver under standard conditions by 0.26 Å.

Cubic phases with the BiF_3 structure are only one example of intermetallic compounds whose formation is accompanied by large volume effects.

Intermetallic compounds formed in the "alkali metal—mercury" and "alkali metal—tin (or lead)" systems and new materials, namely, alloys of alkali and alkaline earth metals with transition metals, *e.g.*, potassium with nickel[17] or calcium with cobalt,[**18**] are equally interesting objects with respect to "supercompressed" state chemistry. Therefore, "chemical pressure" reactions can be considered as a new, quite promising line of research both in structural and synthetic high-pressure chemistry.

Studies making use of the "chemical compression" principle provide valuable experimental data, which contribute to the understanding of the nature of the "supercompressed" state, whose density is several-fold greater than that of a substance under standard Earth surface conditions, 1 atm and 300 K.

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