The stability of solid and liquid compounds with strong anion–anion interactions

W Geertsma

Solid State Physics Laboratory, University of Groningen, Nijenborgh 16,
9747 AG Groningen, The Netherlands

Abstract. The equiatomic alkali-group-IV (Si, Ge, Sn, Pb) compounds usually crystallize in the NaPb structure. This structure contains negatively charged tetrahedra of group-IV ions, which are separated by alkali ions. The Li compounds, however, have either a CsCl (LiSn, LiPb) structure or a structure with a three-dimensional network of group-IV atoms, e.g., LiGe. A similar difference between Li compounds on the one hand, and Na, K, Rb, Cs compounds on the other hand, has been found in the corresponding liquid alloys. We explain this difference in structures in terms of two factors: the existence of a gap in the density of states at the Fermi level in the phase with tetrahedra, and the radius of the alkali atom. When the alkali ion is too small, like Li^+, to separate the tetrahedra, then either the CsCl structure is the most stable, or a threefold-coordinated anion network will be the most stable structure. The latter structure occurs when the group-IV anions have a strong covalent interaction like for Ge and Si.

1. Introduction

The equiatomic alkali (A)–group-IV (B) solid compounds usually crystallize in the NaPb structure. Exceptions are the Li compounds which crystallize either in the CsCl structure (LiSn, LiPb) or in a structure with a three-dimensional network of the B sublattice (LiGe) in which the B atoms have a threefold coordination. Similar differences have been observed for the corresponding liquid alloys. (LiSi probably does not exist.) In these systems one electron is transferred from the alkali to the group-IV atom. In the NaPb structure all B atoms are in charged tetrahedra B_4^{4-}. These tetrahedra are separated from each other by A atoms. Some of these compounds have a structure, which includes a distorted tetrahedral building block. We will not discuss this phenomenon in this paper. The systems containing clusters, e.g. the B_4^{4-} tetrahedra, are insulators. For more experimental details I refer to Meijer *et al* (1985) and van der Lugt and Geertsma (1984, 1987).

Geertsma *et al* (1984) derived a stability diagram (figure 1) which explains the relative stability of the clustering and the non-clustering compounds. In this paper we refine this model to determine the relative stability of the CsCl, LiGe and the NaPb structure.

In order to do this we have to examine the next level of complexity, which involves the consequences of covalent interactions between clusters of anions. First we will briefly review some results of earlier work on this subject (Geertsma *et al* 1984, Geertsma 1985, Dijkstra and Geertsma 1985).
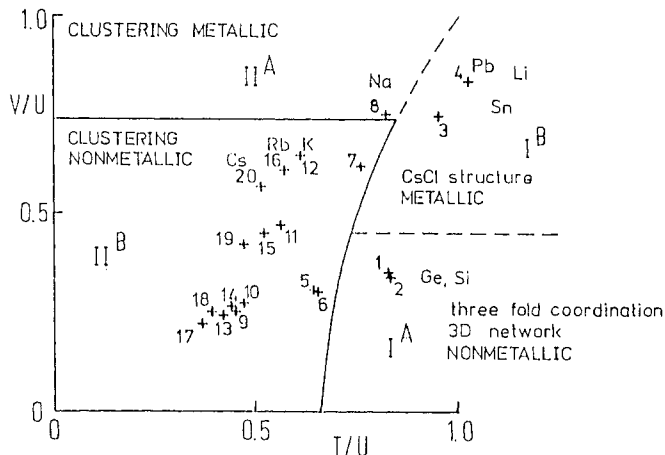
1.0 CLUSTERING METALLIC

II A

Na   4 Pb Li
8 +   +   Sn
V/U   3

CLUSTERING
NONMETALLIC   Cs Rb K   7+   I B
              20 +16 +12
                                CsCl structure
                                METALLIC
0.5
                                        Ge, Si
    II B   19 + +11   1 +2
              18 14 10   5 +   three fold coordination
              + + +   6   3D network
            17 + 13 9   A   NONMETALLIC
                                   I

0
  0   0.5   1.0
              T/U

Figure 1. Stability diagram of equiatomic alkali (A)–group-IV (B) compounds (A = Li, Na, K, Rb, Cs; B = Si, Ge, Sn, Pb) separating clustering (region I) from non-clustering (region II) compounds. Details are discussed in the text and in Geertsma *et al* (1984).

We have shown (Geertsma 1990) that an isolated tetrahedron with fully occupied bonding levels is very stable. However, the valence charges on a tetrahedron repel each other. The isolated charged tetrahedra become unstable in the case of Pb_4^{4-}. In the solid the Pb_4^{4-} tetrahedra are stable because they are embedded in a deep crystalline potential: the Madelung potential of the non-metallic ionic lattice. However, such a strong potential is screened in a metallic system. We predict (Geertsma 1990) a first-order transition in the liquid state for APb. The prerequisite for the existence of these anion clusters in the Pb systems is the existence of a bandgap near the Fermi level, so we will concentrate on this property of the electronic density of states (DOS). In the systems we discuss the valence p states are half-filled, so we have to look for a gap in the middle of the p band. To simulate the atomic structure we use pseudo-lattices. A detailed discussion of these lattices can be found in Geertsma and Dijkstra (1985). The calculation of the electronic structure of liquid alloys with strong chemical bonding is much less developed than that of the corresponding crystalline solid. In order to get insight into the chemical bonding, which determines the structure, we use simple tight-binding models to calculate the density of states. The electronic DOS of a suitable chosen pseudo-lattice exhibits features reminiscent of those found in the bandstructure of the crystalline system (Geertsma and Dijkstra 1985).

This paper is organized as follows. In section 2 we describe the electronic structure and stability of systems with clusters. In section 3 we calculate the electronic structure of the p states of a threefold-coordinated three-dimensional network. In this section we also study the effects of closed transfer paths (loops). The inclusion of transfer loops is of importance to describe structures in the DOS reminiscent of those occurring in the DOS of the crystal (Geertsma and Dijkstra 1985). Secondly, including transfer loops results in a broadening of the DOS with respect to the DOS of a Bethe lattice (figure 3(*b*)). Such loops have to be included in the study of the effects of weak localization of quantum interference on the electronic transport properties. The latter effects are absent in liquids. The main quantity determining the conductivity is the DOS at the Fermi level.
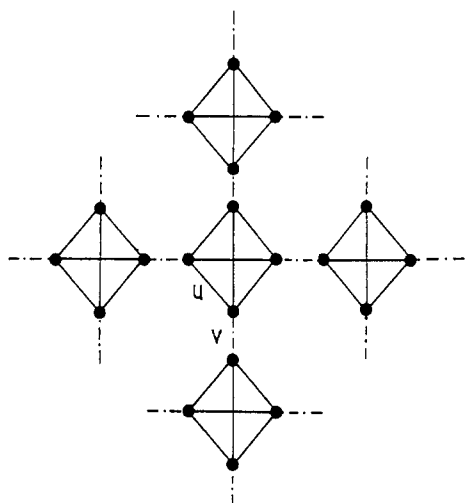
Figure 2. Modified Bethe lattice for $Z_u = 3$ (tetrahedron), $Z_v = 1$. The transfer integral in the cluster is U, while V is the transfer integral between clusters.

Due to disorder transfer loops are also less likely in liquids than in crystalline materials. Section 4 contains a summary and a discussion of the results.

2. The electronic structure and stability of a condensed system with anion clusters

In this section we calculate the condition for the formation of a bandgap for a number of pseudo-lattice models. These pseudo-lattices describe the main features of the anion sublattice (Geertsma and Dijkstra 1985). We may restrict our discussion to this sublattice because the cation states are far above the Fermi level. The principal role of the alkali cations is to keep the anions or the charged tetrahedra apart.

To calculate the electronic density of states we approximate the anion sublattice of the crystalline compounds with a NaPb structure by a pseudo-lattice. For this purpose we constructed the so-called modified Bethe lattice (MBL) (figure 2): the lattice points of a simple Bethe lattice are replaced by a $Z_u + 1$ point cluster; for example for a tetrahedron $Z_u = 3$. Each point of a cluster interacts with Z_v points of different clusters with strength V. The intracluster covalent interaction is U. In figure 2 we give an example with $Z_u = 3$, $Z_v = 1$, that is a lattice of tetrahedra with one bond between corners of two tetrahedra.

For simplicity we take one s orbital per site. Cation orbitals and Coulomb interactions are neglected. We have chosen s orbitals because these can be treated analytically; p orbitals are more difficult to treat and no new physics of importance for the present discussion is obtained. We obtained for general Z_u and Z_v the following condition for the opening of a gap in the DOS:

$$\left(\frac{U}{V}\right)^2 > 4 \left(\frac{Z_v(Z_v - 1)}{Z_v(Z_u + 1)^2 - 4Z_u}\right). \tag{2.1}$$

This condition is 'exact' for pairs $Z_u = 1$: $(U/V)^2 > Z_v$. Note that in the case of a linear chain ($Z_v = 1$, $Z_u = 1$) one always has a gap.

In the first paper of this series (Geertsma *et al* 1984) we have argued that a tetrahedron with p orbitals can be described by a pair cluster with s orbitals by choosing the appropriate Z_v. We have chosen $Z_v = 2$, because this gives the same total coordination of the

pair cluster as found for the tetrahedra in the crystalline structure. The calculated electronic structure is qualitatively similar to the one calculated using the Augmented Spherical Wave method (Springelkamp *et al* 1985). It also agrees with recent calculations using the recursion method (Meijer 1988). This approximation gives the horizontal line in the stability diagram separating the metallic region, with clusters, from the non-metallic region also with clusters (figure 1). Note that only the Li compounds and probably NaPb are predicted to be metallic; all the other compounds are non-metallic, as has indeed been found experimentally.

It would be of interest to extend this calculation to the degenerate p orbitals on covalently interacting tetrahedra. To get some insight into the effects due to orbital degeneracy we have studied a system consisting of two sets of g-fold-degenerate unperturbed states per cluster. For a tetrahedron $g = 6$. On the tetrahedron p orbitals split into a sixfold nearly degenerate set of bonding states and a sixfold nearly degenerate set of antibonding states. These states are separated by $2E_B$. This parameter is similar to the parameter U we used in the case of pairs on a MBL. The clusters are considered as sites on a Bethe lattice. States on nearest neighbour sites hybridize in the following way: V between the same orbitals, V_0 between orbitals of the same set, V_1 between orbitals of different sets. The number of nearest neighbours is Z. For more details see Geertsma and Dijkstra (1985). The condition for the existence of a gap is

$$(E_B/V)^2 > 4(Z - 1)\{[1 + (g - 1)V_0/V]^2 - g^2(V_1/V)^2\}. \tag{2.2}$$

Let us compare this result with that obtained above for s-type orbitals on a MBL. For the case of s orbitals on a pair cluster $g = 1$, one obtains $(E_B/V)^2 > 4(Z - 1)[1 - (V_1/V)^2]$. Note that for $V_1 = V$ one always finds a gap. Also for a linear chain, $Z = 1$, one will always find a gap in the DOS of this model. This result is the same as the one obtained for a pair cluster on a MBL.

Also in the case where all interactions are the same the gap is open. This is due to the second term in the brackets (V_1/V): this interaction between different levels, V_1, pushes these levels apart, and even compensates for the broadening of the individual bands due to the nearest neighbour interactions, V_0, between levels of the same set. From these results we conclude that when one discusses the formation of a band gap, the MBL with the pairs ($Z_u = 1$) with one s orbital per site is a reasonable approximation for threefold-degenerate p states on a tetrahedron.

The results of this paragraph and the previous one on the MBL lattice cannot be compared in all their details, because in the former we took the phase of the wave functions into account in the interaction between nearest neighbours, while in the latter we neglected this. We argue that the MBL model is more appropriate for a crystalline solid, while the latter is more applicable for a disordered system.

Finally we consider some effects which have been left out so far in our discussion of the formation of a gap.

    (i) Dissociation of the clusters.
    (ii) The influence of the cation levels.
    (iii) Chemical short-range order (σ).

These points have been discussed by Geertsma (1985), using a renormalized perturbation expansion of the self-energy up to the second step in the continued fraction. The A^+ and B^- ions and the B_4^{4-} clusters are distributed over the Bethe lattice. The short-range order is described by Warren–Cowley parameters σ_{ij}. Using this approach

one can easily derive the following expression for the formation of a gap in the DOS when we assume the cation orbitals to be far away from the anion orbitals

$$(E_B/V)^2 > 2p_{cc}g(Z-1) \tag{2.3}$$

where $p_{cc} = c_c + c_a\sigma$ is the conditional probability of finding a cluster, next to another cluster. The subscript c refers to the cluster B_n, c_c is the fraction of clusters and g is the number of states of each set of bonding and antibonding cluster levels. This condition differs from the one above, (2.2), because in this approximation one neglects repeated transfer of an electron between two nearest neighbours. In this way a large part of the energy levels shifting away from each other is not accounted for. Secondly, the cut off of the renormalized perturbation expansion results in the well known square root dependence of the bandwidth on the coordination number. The same holds for the degeneracy factor g. When the degeneracy is treated in the right way, as in equation (2.2), it appears as a linear term. Setting $V_1 = 0$ and $V_0 = V$ as done in the derivation of equation (2.3), equation (2.2) gives $E_B > 2\sqrt{(Z-1)}\,gV$.

In equation (2.2) one can replace $Z - 1$ by $p_{cc}(Z - 1)$ so as to incorporate chemical short-range order in that model. In the case of an A_4B_4 ($c_c = 0.2$) alloy the short-range-order parameter becomes for complete order $\sigma = -0.25$, and so $p_{cc} = 0$. In this limit the gap always exists because the clusters are isolated from each other by the cations. In the case of complete disorder $\sigma = 0$, so $p_{cc} = 0.2$. Broadening due to degeneracy of the cluster levels can be compensated by order of the liquid alloy.

From these calculations we learn that in the case of formation of clusters the band width increases with increasing degeneracy of the cluster levels. This broadening is opposed by the short-range order because then short-range order strongly decreases the effective number of nearest neighbours. In the limit of complete order each charged cluster is coordinated by cations with orbitals unavailable for electron transfer; consequently the electron or cluster-type orbitals become narrow. So a gap will appear in the DOS.

3. The electronic structure of a threefold-coordinated network

In this section we consider the DOS of a threefold-coordinated network as an idealized model (figure 3(a)) for the three-dimensional network of Ge in LiGe. The corresponding pseudo-lattice models used for the simulation of the structure are in figure 3(b), (c). On each site we have three p orbitals: one p orbital has a σ bond V_σ with a p orbital on a nearest neighbour site and the two others have a π bond V_π with the other two nearest neighbours. The sticking of the sites is in such a way that when one neglects the π bonding only *isolated* σ bonded pairs remain. In the discussion below we will again emphasize the conditions for the formation of a bandgap at the Fermi level. We neglect closed transfer paths like the path ABCDEF in figure 3(a), but preserve the right order of π and σ bonds, and also the nearest neighbour coordination number. The simplest pseudo-lattice corresponding to this lattice (figure 3(a)) is given in figure 3(b). One can derive for the DOS

$$n(E) = -(1/\pi)\,\text{Im}\,1/(E - T_\sigma V_\sigma - 2T_\pi V_\pi) \tag{3.1}$$

where $T_\sigma = V_\sigma/(E - 2V_\pi T_\pi)$, and T_π is given by the solution of

$$(ET_\pi - V_\pi - V_\pi T_\pi^2)(E - 2T_\pi V_\pi) - V_\sigma^2 T_\pi = 0. \tag{3.2}$$

A gap will open in the DOS if

$$V_\sigma/V_\pi \geqslant \sqrt{2}.$$

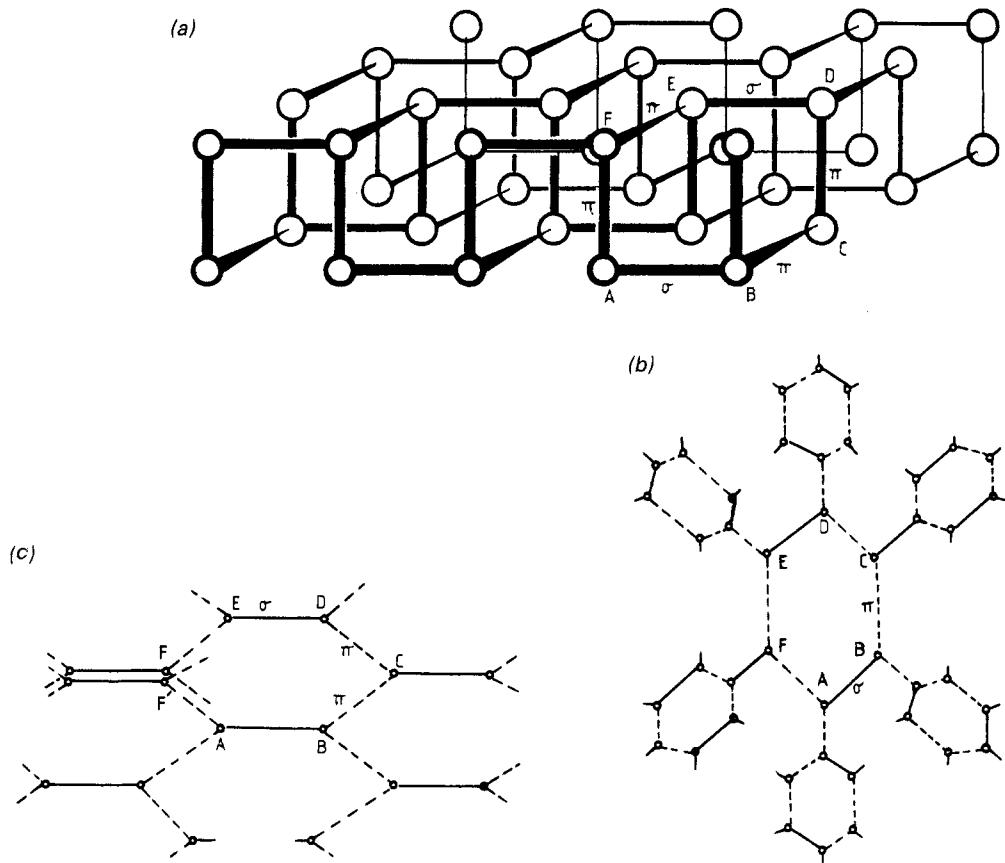This transfer matrix method is on this level of approximation equivalent to cutting

Figure 3. (*a*) Lattice model for a threefold-coordinated network. (*b*) Schematic two-dimensional representation of a pseudo-lattice corresponding to this lattice (figure 3(*a*)), without closed transfer paths. (*c*) The corresponding pseudo-lattice including the shortest hexagonal closed transfer paths.

of the renormalized perturbation expansion or continued fraction expansion at the second step (pair approximation).

We have also studied the influence of taking into account shortest closed transfer paths ABCDEF in figure 3(*a*), using the renormalized perturbation expansion. The pseudo-lattice retaining the coordination number and the order of π and σ bonds, corresponding to the real lattice (figure 3(*a*)), is given in figure 3(*c*). Note that only part of these shortest loops can be taken into account because each bond is shared by two tilted hexagonal closed transfer paths. The results with and without taking into account the lowest-order closed transfer path (of order $V_\sigma^2 V_\pi^4$), are presented in figure 4. Closed transfer paths suppress the formation of a gap.

To study the influence of *inter*layer interactions we assume that each atom has a one-electron interaction W with three nearest atoms in another nearby layer. We neglect closed transfer paths. The results of the formation of a gap are given in figure 5 ($V_\sigma/V_\pi = 4$). For $W > 0.5\,V_\sigma$, we find that the gap closes, thus resulting in a metallic system. A structure with a high coordination number is usually favourable for metals. Furthermore we have plotted in the same figures the density of states in the middle of
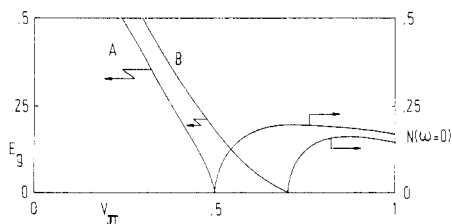
Figure 4. Gap (E_g) in the DOS as a function of π bonding for $V_\sigma = 1$, and DOS in the middle of the band ($N(\omega = 0)$): A: without transfer loop; B: with transfer loop.
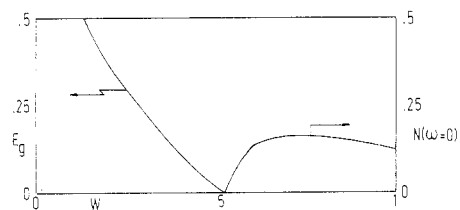
Figure 5. Gap (E_g) and density of states $N(\omega = 0)$ as a function of the interlayer interaction W for $V_\pi/V_\sigma = 0.25$; interlayer coordination number $Z = 3$.

the band. This density of states first increases strongly with increasing W or V_π and then decreases. Harrison (1980) finds rather generally $V_\sigma/V_\pi = 4$, so we predict that as long as interlayer interactions can be neglected a gap will open in the density of states.

Let us now study the stability of this lattice for half-filled p orbitals. In the limit of small π bonding this can be easily done: the isolated σ bonds have a stabilization energy of $-2V_\sigma$ per pp$_\sigma$ bond at half filling; the total number of such bonds in the lattice is $3N$ (N is the number of atoms), so the stabilization energy is $-3V_\sigma$ per atom. This is somewhat larger than the stabilization of a tetrahedron ($-2.67\ V_\sigma$ per atom, see section 2). The covalency parameter is inversely proportional to the interatomic BB distance. So when the B$^-$ ions can, on the average, come closer to each other in the threefold-coordinated network than in the clustering structure, the first structure has a lower energy than the clustering structure. This is what happens in the LiB compounds. For all the other alkali compounds (A = Na, K, RB, Cs) the distance between the B$^-$ ions becomes too large to stabilize the network with respect to the clustering structure.

The next question one has to answer is: when is this network structure more/less stable than the three-dimensional CsCl-like structure of LiPb and LiSn. The stability of the network derives from the opening of a gap in the DOS in the Ge and Si compounds. This is not possible in the case of the Pb and Sn compounds. Madelung contributions to the stabilization of the structure play an important role in the case of non-metallic systems. These contributions are probably of importance in LiGe. This question will be treated in more detail in a separate paper (Geertsma 1990).

This correlation between closing of the gap and change in structure is also observed in the sequence of the isoelectronic P, As, Sb, Bi. All isomorphs of P are non-metallic while Bi is metallic with a structure with a high coordination number. As and Sb have layered structures with a threefold coordination; however, with increasing atomic weight the ratio of the *interlayer* interactions to the intralayer interactions increases and closes the covalent gap. Interlayer interactions are of the same magnitude as the intralayer interactions, especially for the heavier metalloids (Bellisent *et al* 1987, Gaspard *et al* 1987).

4. Summary and discussion

We have studied the stability of solid compounds with strong anion–anion covalency. The lattice is simulated by pseudo-lattices to take into account the principal characteristics of the real lattice: coordination number, local symmetry. Geertsma and Dijkstra (1985)

have shown that such an approach for the calculation of the electronic DOS describes its main characteristics: singularities (van Hove, logarithmic), bandgaps. Only the bandwidth is suppressed and sometimes spurious localized states are found outside the band. This approach gives a good approximation for the total one-electron energy as it incorporates a number of the lowest moments of the DOS. In the case of the tetrahedron structure closed paths of the order $(UV)^4$ and in the case of the three-dimensional network closed paths of the order $V_\sigma^2 V_\pi^4$ are neglected. The difference in the structure of LiGe and the NaPb structures is mainly attributed to the cation radius. The Li^+ radius is too small to separate anion tetrahedra, while it is small enough to support a three-dimensional threefold-coordinated network of Ge.

A more genuine application of the model presented in this paper is to the structures of the post-transition metal elements as in this case Coulomb interactions do not play an essential role determining the energy difference between structures. The heavy post-transition elements like Sn, Pb, Sb, Bi crystallize in a metallic phase, while the light elements of this group crystallize in an insulating phase (Si, Ge, P, As, S, Se). The difference in structures can be understood in terms of the large coordination numbers of the metallic phase, thereby lowering the kinetic energy of the valence electrons, and low coordination numbers of the non-metallic system with strong covalent bonding, so enhancing the stability of the bonding bands.

The stability diagram for the equiatomic alkali-group-IV compounds (figure 1) is divided into four regions. In region II^A the covalent interactions within the tetrahedra are strong and so cause a splitting in the valence band in a bonding and an antibonding band. These compounds are solid state semiconductors. In the liquid state these compounds have a very high resistivity. The compound NaPb is on the borderline between the regions with clusters and without clusters. In the solid state one observes the Pb_4^{4-} tetrahedra, while in the liquid only a small fraction of the Pb ions are in clusters. Region I is divided into a region with weak interactions between the anions: LiPb and LiSn, and a region with strong interactions between the anions: LiGe and LiSi. The first have a CsCl-like structure and are metallic, while the anions in the second compounds form a three-dimensional network. In the liquid state LiPb and LiSn have a low resistivity, while the resistivity of liquid LiSi and LiGe is in the region of diffusive motion.

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