POLARIZATION AND STRUCTURE OF SMALL CLUSTERS.

W. GEERTSMA,
Departamento de Fisica, UFES, Av. Fernando Ferrari s/n
Vitoria–ES, Brasil.
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Abstract

In this paper we report the structure of the Li$_4$Ge$_4$ cluster as a function of charge transfer and polarizability. We find that for small charge transfer ($Q < 0.5$) this cluster has the expected cubic structure: a Ge$_4$ tetrahedron with a Li ion attached at large distance to each face. With increasing charge transfer $Q > 0.5$ the structure of Li$_4$Ge$_4$ changes: for relative small polarizability of the Ge ion the Ge$_4$ breaks up into two Ge$_2$ pairs separated by the four Li. For larger polarizability there are three possibilities: 1) for full charge transfer the Li ions break up the Ge subcluster into four separated ions; 2) for smaller values of the charge transfer we still have the structure with two Ge$_2$ pairs and 3) for intermediate values of, charge transfer the Ge sublattice forms a structure with two opposite bonds of the Ge$_4$ tetrahedron cluster broken. These are the only stable geometries found. For large Ge polarizability we find that all structures become unstable: the size of the induced dipole moment becomes larger than the diameter of Ge. Based on this phase diagram of Li$_4$Ge$_4$ we discuss the structure of other A$_4$M$_4$ alkali(= A)–tetalide (= M) (= group 14) clusters, and related solid state structures.

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1 INTRODUCTION.

In this paper we study the influence of polarization on the structure of small ionic-covalent clusters. In a previous paper [1] (to be referred to as I) on this subject we have reported that polarizability can be an important factor determining the geometry of clusters, especially clusters consisting of electropositive and electronegative atoms. We illustrated this by the calculation of the structure of $A_4M_4$ clusters where $A$ is an alkali ion: Li, Na, K, Rb, Cs and $M$ is a tetrалide ion: Si, Ge, Sn, Pb as a function of the polarizability. We used the full ionic charges in these calculations. We find that the structures are only stable for polarizabilities smaller than about 0.7 times the Fraga [2] values. Secondly, we find that for this maximum value of the polarizability the stable structure of $K_4M_4$, $Rb_4M_4$ and $Cs_4M_4$ is a $M_4$ tetrahedron with the alkali far outside the four faces of this tetrahedron: the Normal Double Tetrahedron (NDT) structure. We found that in case of Li and Na for small polarizability of $M$ the same structure as for the other alkalis, while for large values of the polarizability we found the Li or Na near the faces of the $M_4$ tetrahedron: the Near Face Centered Double Tetrahedron (FDT) structure. For intermediate values of the polarizability we find two pairs of $M_2$, separated by Li or Na (to be indicated by PAR) and a boat or butterfly like structure: a tetrahedron with two elongated opposite $M$–$M$ bonds, we indicate by BUT. Note that NDT and FDT have $T_d$ symmetry, and PAR and BUT have $S_4$ symmetry. One can continuously distort the first structures to get the latter structures, $T_d$ is a special case of $S_4$ symmetry.

In the present paper we will discuss these clusters in some more detail, with especial emphasis of the dependence of the geometry on the ionic charge and polarizability. In the calculations we reported in I we also found sometimes a structure with the $M$ ions in a sort of butterfly geometry (indicated by BUT). However we always found this geometry to have a smaller binding energy than the other geometries for the $M$ subcluster: two $M_2$ pairs (PAR), the Normal Tetrahedron (NDT) and Near Face Centered Tetrahedron (FDT). However the difference in binding energy was rather small (of the order of 0.1 eV). So we decided to study the dependence of the structure of these clusters on the ionic charge. Another reason to look whether the geometry depends on the ionic charge is that we found in I from our semi-empirical quantum calculation on these clusters that the charges on the ions are somewhat smaller than the full ones.
Furthermore, we note that there are two structures for crystalline LiGe \cite{3}: one equivalent to LiSi (a Si network with a three–fold coordination) and a second one with weakly coupled layers of Ge, with half of the Ge with a four–fold coordination and the other Ge with a two–fold coordination. This would lead to charge imbalance, with one neutral Ge and one Ge$^{2-}$. An analysis shows that the latter Ge has two rather short interlayer Ge–Ge bonds, which have a bond strength \cite{4} of 0.25 each, so its formal valence charge is Ge$^{1.5-}$, thus satisfying the generalized Zintl-Bussmann-Klemm valence rule \cite{5}. The other alkali monotetralides crystallize either in a structure with well defined M$_4$ tetrahedra (all Na, K, Rb, Cs monotetralides) or in a structure with M layers (LiSn) or in a distorted CsCl structure (LiPb). These structures are reviewed in \cite{6, 7}. The only known IR spectra are reported in \cite{8}.

This is not the only known structure where the tetralide M$^-$ ions form layered, three–dimensional network or a structure with isolated tetrahedrons. Earth-alkaline ditetralides crystallize all in a structure with three–fold coordinated tetralide sublattice \cite{9} in a layered structure (CaSi$_2$, High-Pressure-High-Temperature BaSi$_2$) or in a structure with tetrahedra (BaSi$_2$, CaGe$_2$, SrGe$_2$, BaGe$_2$), or in a structure with a three–dimensional network (SrSi$_2$). Large cations seem to favor the structure with tetrahedra, small cations the layered structure.

We choose to study the structure of Li$_4$Ge$_4$ as a function of polarizability and ionic charge. In the next section we give a brief account of the theoretical model. In section 3 we give results, in section 4 we give a discussion of these results and the conclusions.

2 THEORY.

The theoretical model we use is the same as in I. It is a mixture of a semi–empirical quantum mechanical model and a classical electrostatic model. The semi–empirical model is used to describe the valence electrons. It is basically an adaptation for clusters of the parameterization scheme given by Harrison \cite{10, 11} for the hybridization matrix elements he derived for the solid state. We have applied his new scheme \cite{11} and parameter values, which includes overlap matrix elements calculated by the Wolffberg–Helmholtz approximation. Electron–electron interactions are neglected in this scheme. The unperturbed atomic orbital energies are also taken from
We include the peripheral s state correction as a perturbation. We include only the atomic s and p levels of the alkali and tetralide.

The classical electrostatic contributions to the binding energy consist of the Coulomb interactions of the ionic charges \((Q)\), the interaction between the Coulomb fields and the induced polarizability, the dipole-dipole interactions, and the energy required to create these induced dipoles. The polarizability is taken from Fraga \([2]\). All results are reported as a function of the fraction of these polarization values. The polarizability of A and M are determined by the same fraction of the Fraga value.

Next to this we have two semiclassical contributions: the van der Waals interaction and the Born repulsion. For the first we take the form: \(C/R^6\). The constant \(C\) is approximated by the polarizability. As this contribution is in general small we did not optimize the parameter \(C\). For the Born repulsion between two atoms/ions 1 and 2 a distance \(R\) apart we take:

\[
F(\rho_1 + \rho_2) \exp((R_{i0}^0 + R_{j0}^0 - R)/(\rho_1 + \rho_2)),
\]

where \(R_{i0}^0\) is the Born radius of atom \(i\), and \(\rho_i\) is the decay length of the Born repulsion for \(R > R_{i0}^0 + R_{j0}^0\). The Born radii have been fixed so as to reproduce the neutral atom interatomic distances (see \([12]\) and I) by this model.

We do not take into account the contribution due to the covalent distortion of the valence electron density in the calculation of the polarization contribution. We also neglect the distortion of the core charge density due to core–core overlap in case of short interatomic distances.

We have calculated the minimum energy using the Simplex method, using all atom coordinates in the minimization. In some cases, to be discussed below, we have used structures with a fixed geometry: NDT and FDT with two parameters, PAR and BUT with four parameters.

### 3 RESULTS AND DISCUSSION.

In figure 1 we present the cluster structure phase diagram for Li\(_4\)Ge\(_4\). We find five regions: one where the tetrahedron of Ge is stable (NDT), one where Ge\(_2\) piars are stable (PAR), another where a butterfly geometry - a tetrahedron with two long opposite bonds - is stable (BUT) and a fourth where isolated ions of Ge are stable (FDT). These structures are illustrated in figure 2. The fifth region for \(\alpha > 0.75\alpha_F\) is where the \(A_4M_4\) can always find a configuration in which
the polarizability becomes the most important contribution to the total energy. We illustrate these geometries in figure: 2 for the Li4Ge4 cluster.

Let us first discuss the extent of the latter region of instability. It has been known for a long time that including the polarizability of ions in the calculation of the cluster structure with minimum energy can give rise to divergences in the total energy. Some years ago, Thole [13] discussed the problem of the polarization catastrophe in Molecular Dynamics simulations of molecules due to close approach of two molecules. He derived a criterion for the nearest approach of two molecules in order to avoid such problems: the effective polarizability of two polarizable molecules diverges if two molecules approach each other closer than \( R = (2\alpha)^{1/3} \). This criterion is independent of the local electric fields. However, using this criterion our systems would be stable.

We performed a calculation for the butterfly/pair geometry of the total energy, and derived a relation between \( R \) distance in the pairs (or the diagonal, in the butterfly) and the distance between the pairs (height of the butterfly): \( H \). One then finds the following condition for divergence of polarization contribution to the total energy:

\[
A = \frac{R^3}{\alpha} = \frac{1}{4} \left[ x - 2 + \left( (3x - 2)^2 + 16\frac{H^2}{R^2}x^2 \right)^{1/2} \right] \tag{1}
\]

where \( x = (1/2 + (H/R)^2)^{-5/2} \). We find that for \( R \leq (4.66\alpha)^{1/3} \), there is always an \( H \) for which the total energy diverges. Using the values of Fraga for the polarizability, we find that the critical value of the polarization is \( \approx 0.7\alpha_F \). This is what we actually find in our simulations. This limit for stable solutions is independent of the electric field. Obviously within this region of polarization induced instability there are relative minima.

In this instability region we find that for certain atoms the length of the dipole moment is larger than the ion diameter. The polarization energy becomes even larger than the Born repulsion, and the ions can come very close together. Our model is not longer valid: The cores start to overlap strongly, and one should also take into account the deformation of the core charge distribution, described by the so-called deformation dipole moment (Tosi et al [14]).

In the region where we find the stable geometries we can describe the succession of structures with increasing polarizability as if polarizability tends to break the covalent M-M bonds: large
polarizability together with strong electric fields act as a scissor on covalent bonds. Also from the point of view of increasing the ionic charges one finds these covalent bonds are broken with increasing ionic charge: from a Ge$_4$ tetrahedron in the NDT structure with six Ge–Ge bonds with a length of approximately 2.53 – 2.61 Å with the Li far away outside on its 4 faces, to a BUT structure with a Ge$_4$ butterfly with four short Ge–Ge bonds (2.45-2.53 Å), and two long “bonds” of about 3.00 Å. This geometry is for relative large polarizability an intermediate structure to a PAR structure with two Ge$_2$ pairs, with a total of 2 Ge–Ge with bond lengths of 2.39 – 2.45 Å. These pairs are about 3.68 – 3.80 Å apart. For relative large polarizability the Ge pairs further dissociate to isolated Ge ions (FDT), where one finds the four Li on or just outside the faces of the large Ge tetrahedron. In this case the interatomic Ge distance is about 3.7 Å.

In the stable regime we have applied the Simplex to minimize the total energy with all atom coordinates. In some cases one has to be very near to the minimum otherwise the Simplex gets stuck in a relative minimum. This happens especially in the case of two pairs. One of the problems is that there are two solutions with pairs in the case of Li$_4$Ge$_4$, which are separated by an energy of about 0.7 eV. The one with highest energy has a somewhat larger Ge–Ge distance in the Ge$_2$ pairs. Secondly, in case of the pairs with lowest energy, the energy minimum in the coordinate “landscape” seems to be very localized, and difficult to find. Such a problem did not arise for the other geometries of Li$_4$Ge$_4$.

We have calculated the vibration energies (which we report elsewhere [12]) of these clusters. We find that the cluster with two pairs with the short Ge–Ge bond has one mode with a very large energy of the order of 0.8 eV. We noted that the Simplex has difficulties finding the minimum, and actually one finds a number of saddlepoints which are very close in coordinate space. Note also the large extend of the region in the phase diagram where the Ge$_2$ pairs are metastable $\square$B.

We find that the ionic charges as calculated from the semi–empirical molecular orbital part of our calculation are approximately 0.8 for all A$_4$M$_4$ clusters.

In the solid state we identify the M$_4$ tetrahedron binding energy with the energy difference between the NDT and FDT configuration. We calculated the energy difference between a A$_4$M$_4$
cluster with a M₄ tetrahedron (NDT) and with four isolated M ions (FDT). For the charge transfer we take \( Q = 0.8 \) and for the polarizability \( \alpha = \alpha_F \). The results are in table [1] and where they can be compared with results from an analysis of lattice energies [2] and with M₄ binding energies derived from specific heat data [10]. Note the good agreement of the energy differences calculated within our simple model and the binding energies obtained from the specific heat data [10] and Madelung energy analysis [4].

4 DISCUSSION AND CONCLUSIONS.

Using this relative simple model, introduced in section 2, for the calculation of the total energy of ionic-covalent clusters, we have studied the influence of the polarizability on the geometry and structure of a relative simple cluster Li₄Ge₄. We find that polarizability together with ionic charge can break covalent bonds. This is contrary to the usual believe that polarization plays approximately the same role as covalent bonding. Strong polarizability breaks covalent bonds. In order to access the validity of our model for these A₄M₄ clusters we also calculated the dissociation energy and vibration energies [12] of these clusters. Where experimental data are available we find good agreement with experiment.

A region of instability in the phase diagram of Li₄Ge₄ clusters is found for large polarizability. The most simple way to remedy the deficiency of our model is to introduce the deformation dipole, which develops when two atom cores are overlapping.

From the phase diagram of LiGe [1] we conclude that for small anion polarizability these Li₄Ge₄ clusters have a cubic structure with anions and cations approximately on the vertices of a cube, independent of the ionic charge. For increasing anion polarizability the Ge₄ tetrahedron deforms into two pairs, separated by the four Li cations, or into a butterfly, with two relative long M–M bonds, and four normal M–M bond lengths, or into a structure where all the covalent bonds of the Ge₄ tetrahedron are broken up. Further increasing the polarizability we enter into a regime where no structure is stable. In case of Sn and Pb we do not find these intermediate phase of pair or butterfly.

Let us now briefly comment on how we can apply this results to solid state structures. In
general we expect the local Coulomb fields in a solid to be smaller than in the clusters we have studied. In order to apply our results to the solid state we have to keep this in mind. Firstly, for small cations like Li and Mg we donot expect isolated $M_4$ tetrahedra in the solid state – unless when $\alpha_M$ is very small. A possible characteristic for the structure of these compounds are in this case: a 3–fold coordinated 2d or 3d network of the M sublattice or a strongly distorted ionic structure (NaCl, CsCl).

Secondly, For large cations like K, Rb, Cs, Ba one expects based on the calculations presented in this paper isolated $M_4$ tetrahedra. Na, Ca and Sr are intermediate. In our very first paper [15] on this subject we applied a simple hybridization model to a modified Bethe lattice. We found a very clear separation between the isolated tetrahedron structures of Na, K, Rb and Cs mono tetralides and the Li monotetralides. The different structures found for these Li compounds can only be explained by taking into account polarizability.

It is clear that one finds the same trends in the solid state as found for these small clusters. The pair and butterfly configuration can be compared with the 2–dimensional layered and 3–dimensional network structures found for LiGe and LiSi.

Next let us turn our attention to the liquid state of these alkali mono tetralides. For reviews of this field see: [17]. LiSn and LiPb are not of interest because the tetrahedra are already broken up in the solid state. In the liquid state of Cs, Rb and possibly K monotetralides one finds tetrahedra, which, due to entropic effects, break up with increasing temperature into smaller units. This holds probably also for NaSn and NaPb. This is actually the interpretation of the Schottky anomaly found in the liquid state of these systems [16]. In case of NaSi and NaGe there is also the possibility of the formation of 3-fold coordinated network: in our calculations the BUT and PAR configurations are metastable phases with an energy not far above the NDT. This offers also an explanation for the occurrence of these M networks observed in MD [18, 19] and Reverse Monte Carlo [20] simulations.

We conclude that these model calculations on small ionic–covalent clusters can give us reliable data on the interatomic distances, binding energy and vibration spectra of such small clusters, and is a basis for the discussion of structural phase transitions in alkali-monotetralides and alkaline–earth–ditetralides.
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Table 1: The binding energy (eV) of tetralide tetrahedra. A: derived from the energy difference between the NDT and FDT geometry as described in the main text. B: derived from the best fit to specific heat data (see [16]). C: Derived from lattice energy difference taken from [8].

|       | KSn | RbSn | CsSn | KPb | RbPb | CsPb |
|-------|-----|------|------|-----|------|------|
| A     | 1.8 | 2.4  | 2.5  | 0.9 | 1.5  | 1.7  |
| B     | 1.8 | 2.0  | 2.0  | 1.6 | 1.5^5| 1.7  |
| C     | 1.7 | 1.80 | 1.97 | 1.4 | 1.54 | 1.67 |
Figure 1: In this cluster phase diagram (A) we give the various stability regimes of Li$_4$Ge$_4$ as a function of ionic charge ($Q$) and polarizability $\alpha/\alpha_F$. The dotted line in the BUT region separates the metastable PAR from metastable NDT in the BUT region of the phase diagram. In the B we show the extend of the metastable PAR phase. For more details see the main text.

Figure 2: The Li$_4$Ge$_4$ cluster structures: NDT; PAR; BUT; IDT.
Geertsma Fig 1A

Geertsma, Fig 1B
Geertsma, Fig 02