

LOCAL ELECTRON DENSITY MODELS FOR Tl TO Pb CONVERSION IN LORANDITE

I. GRŽETIĆ

Faculty of Mining and Geology, University in Belgrade, University Laboratory for Electron Microanalysis, 11000 Belgrade, Yugoslavia

The nuclear conversion of ^{205}Tl to ^{205}Pb by neutrino capture, lorandite (TlAsS_2) converts into Pb-bearing lorandite ($\text{Tl}_{1-x}\text{Pb}_x\text{AsS}_2$) where x is a very small number.

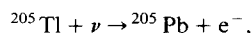
Having used a highly simplified cluster model of lorandite, we intended to calculate the electron density of Tl and its neighbouring atoms by the quantum chemical discrete variational method [5,6].

Substituting Pb for Tl in the lattice site of Tl and calculating the difference existing between these two clusters, we would like to discuss the possible changes of the cluster's stability and the relative binding between Tl-S and Pb-S in lorandite.

1. Introduction

Solar neutrino detection is faced nowadays with several unsolved questions when the processes occurring on the Sun are in question and problems connected with the way in which the neutrino is or will be detected on the Earth.

The isotope of ^{205}Tl has proved to be a convenient solar neutrino detector due to its low neutrino capture energetic threshold (45 keV), although the time needed for the performance of a sufficient number of captures, according to the following reaction,



requires utilization of a detector that contains as high a Tl concentration as in lorandite from Allchar (Yugoslavia) [1].

The lorandite that contains in its lattice traces of Pb at sites of Tl results from conversion of ^{205}Tl to ^{205}Pb . Such lorandite (TlAsS_2) will have a new $\text{Tl}_{1-x}\text{Pb}_x\text{AsS}_2$ formula. We were interested in the very stability of a lorandite crystal lattice and its possible destruction or increment in the lattice energy followed by the appearance of Pb atoms in a lattice, as well as in effects that might result from the change of a lorandite lattice caused by diffusion of Pb atoms out from the inner part of a crystal towards its surface.

The aim of this paper from a purely crystallochemical point of view is the investigation of the influence of trace elements on lattice properties, particularly the changes caused by inserting Pb atoms in the lattice of the host mineral – lorandite. Investigation of this process was possible due to application of the appropriate quantum chemical theoretical approach to an adequate mineral model.

2. Experiment

The three quantum chemical programs SCF- X_α [2], LMTO [3] and DVM [4–6] * were at our disposal. The decision which of the mentioned programs would give us optimal results regarding the geometry of the lorandite lattice and possible models were made balancing the efficiency to reproduce the geometry of the mentioned mineral and the length of the computing time.

As is known, lorandite belongs to a $P2_1/a$ space group that must be simplified when utilization of any of the mentioned programs is concerned and, further, calculations are possible for clusters only, not for an infinite lattice. Comparison of the mentioned programs proved that LMTO requires a long computing time and enormous matrix space to compute the offered cluster. In our decision which of the two remaining programs to choose, the crucial fact was that the DVM method offers better results in the case of open structures where the covalent character of the chemical bond predominates as in sulphosalts like lorandite. This kind of problem can be handled by non relativistic calculations with frozen inner electrons and no cluster relaxation and application of a Watson sphere in order to perform both neutralization and stability of a negatively charge clusters.

This program provides us with the following results:

- coefficients of LCAO for the corresponding molecular orbitals,
- proper electron function values,

* SCF- X_α = self-consistent field - X_α clustered wave cluster molecular orbital method.

LMTO = linear muffin tin orbitals.

DVM = discrete variational method.

- distribution of electron densities within the inter-atomic space encompassing the atoms, valent regions in a cluster,
- a graph of electron densities in a given plane, and
- electron level densities.

Among the presented results we were particularly interested in those regarding electron densities.

3. A simplified lorandite structure

The lorandite structure was determined in 1973 by Fleet [7] and therefore we shall not discuss here the already known structure, but shall focus our attention on the simplification of the mentioned mineral to a model that was acceptable for calculation by DVM.

The symmetry most similar to the original lorandite $P2_1/a$ symmetry is C_{2v} . Within the framework of this symmetry a cluster TlS_7^{-13} with Tl^+ as a central atom $(0, 0, 0)$ and $7S^{-2}$ distributed around the central atom was noticed. Sulphur atoms were arranged in such a way that one atom is located on the Z axis at a distance of 0.322 nm $(0, 0, 0.322)$ and four other sulphur atoms are located in a square arrangement in the $x-y$ plane $(-0.228, -0.228, 0)$, $(0.228, -0.228, 0)$, $(-0.228, 0.228, 0)$ and $(0.228, 0.228, 0)$. The last two sulphur atoms are placed in the $y-z$ plane $(0, 0.228, -0.296)$ and $(0, -0.228, -0.296)$ at a distance of 0.374 nm from the central atom. As is evident from fig. 1 Tl and 5S (at a distance of 0.322 nm) lie within a layer having cubic symmetry and the remaining two S atoms at a distance of 0.374 nm lie in a neighbouring layer of the same symmetry, but which is shifted in such a way that a projection of Tl ions from one layer falls into the center

of a square side of another layer. During conversion of ^{205}Tl to ^{205}Pb , the Pb atom occupies the site of Tl in the cluster so that the new PbS_7^{-13} cluster is identical to the old one, and the difference between these two clusters is only in the electron configuration of Tl and Pb.

4. Obtained results

The total amount of valence electrons in a TlS_7^{-13} cluster is 58 and 59 in PbS_7^{-13} . The difference between these two clusters can be most clearly seen from the results of electron density analysis which refer to valence electrons as the inner electrons are frozen. This means that all the changes are studied on the basis of a different distribution of the total amount of electrons (58 and 59) in two different clusters having the same lattice geometry. This redistribution is determined in the following way. A space net of spots is generated within the clusters and the electron density [4] is determined by a discrete variation method for each spot.

The electron densities characterizing TlS_7^{-13} and PbS_7^{-13} clusters in the $x-y$ plane, encompassing a metal and 4 sulphur atoms at a distance of 0.322 nm, are presented in figs. 2 and 3. The analysis of electron densities indicates the following:

- the relative electron density within a cluster is higher along the y axis than along the x axis, as the presence of the two S atoms (fig. 1) which lie in the $y-x$ plane influence the electron density between a metal (Tl or Pb) and S ligands in the $x-y$ plane,
- the electron density of the TlS_7^{-13} cluster is redistributed in a different way when compared to the PbS_7^{-13} cluster.

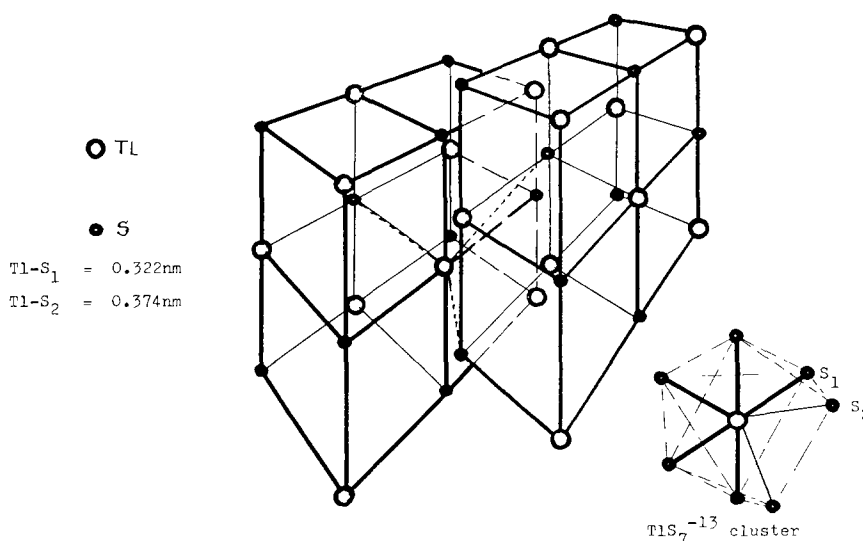


Fig. 1. A simplified structure of lorandite ($TlAsS_2$).

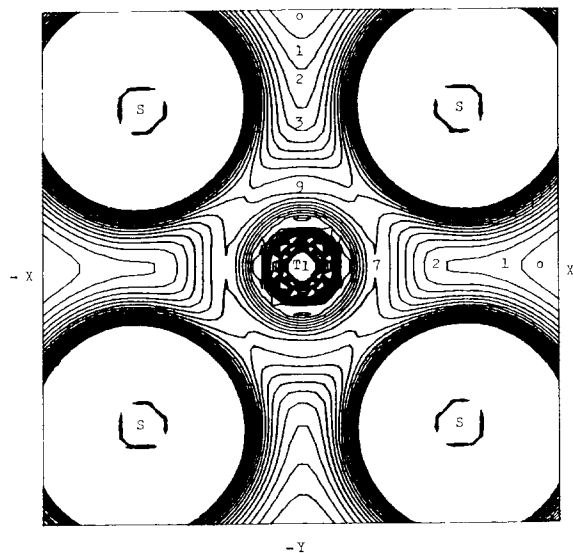


Fig. 2. TlS_7^{-13} cluster, electron density plot in the $x-y$ plane

In fig. 4 the difference in electron density between these two clusters is represented. Part of a field with a negative value indicates a far higher electron density near Pb than in the vicinity of Tl, but on the other hand a positive value penetrating deep into a cluster along the y axis is also evident. This suggests that in TlS_7^{-13} the charge density is probably higher in the $y-z$ plane than in PbS_7^{-13} .

In order to confirm the above mentioned statement we investigated electron densities within this plane. Figs. 5 and 6 show electron densities within TlS_7 and PbS_7 clusters. In this connection it should be mentioned

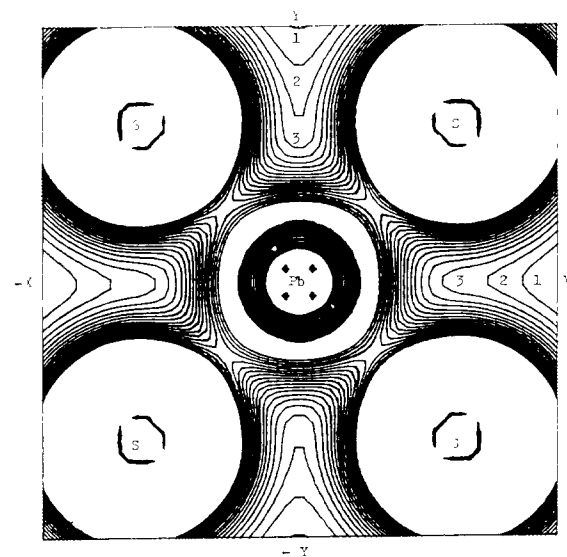


Fig. 3. PbS_7^{-13} cluster; electron density plot in the $x-y$ plane.

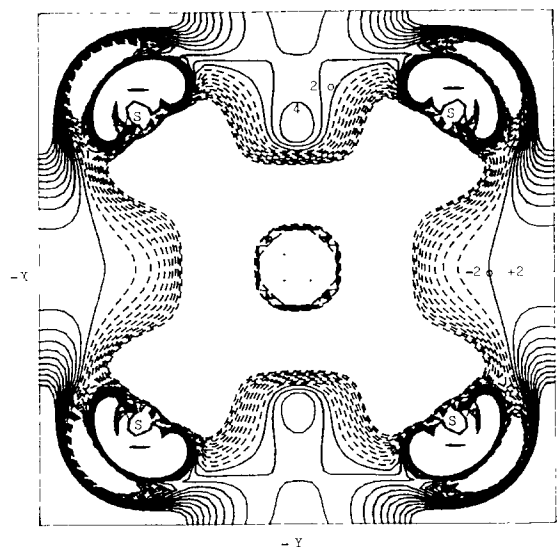


Fig. 4 Difference in charge density between TlS_7 and PbS_7 . (Dashed lines represent negative contours and full lines represent positive contours.)

that one of the S atoms, the very one that lies on z the axis, is located at a distance of 0.322 nm from the central atom, while the other two are located at a distance of 0.374 nm from the central atom. The cross-hatched surfaces given in figs. 5 and 6 are fields of the same electron density and their different extension partly results from the presence of 4S atoms in the $x-y$ plane (although they are out of frame in the given figures) and partly from the various natures of the clusters.

The coordination number 7 in case of the Tl atom represents a common coordination of this heavy metal.

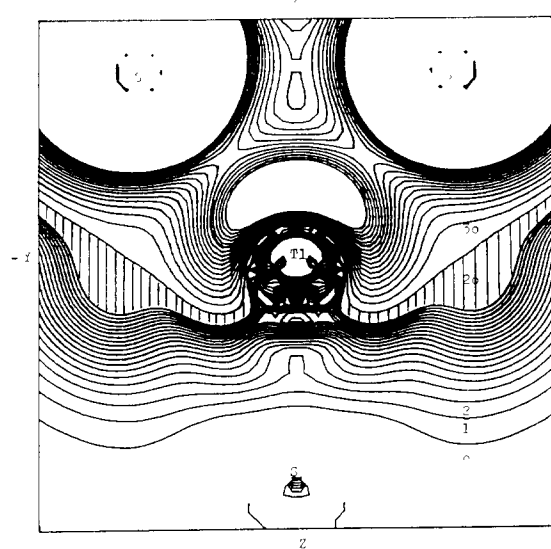


Fig. 5 TlS_7^{-13} cluster; electron density plot in the $y-z$ plane.

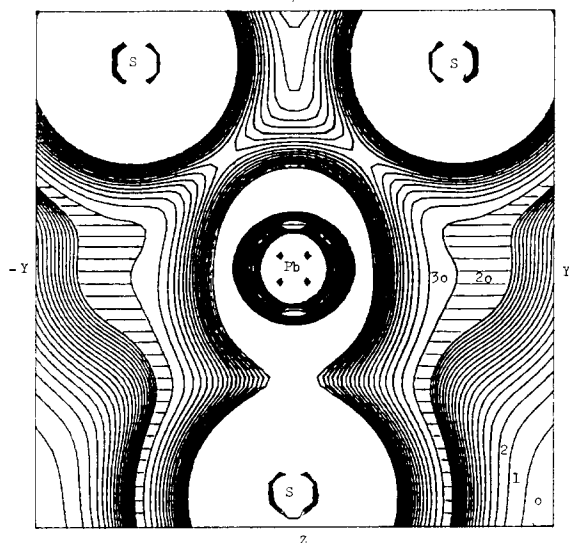


Fig. 6. PbS_7^{-13} cluster; electron density plot in the $y-z$ plane. (The cross-hatched surface is of the same density as the one in fig. 5.)

The voluminosity of the electron shell and the presence of one unpaired electron in the 6p orbital of $_{81}\text{Tl}$ give preference to asymmetric coordination media. Contrary to thallium, $_{82}\text{Pb}$ is characterized by one electron pair in the 6p orbital which certainly influences Pb to form compounds where it is located in a coordination geometry which is almost always based on the galenite crystal lattice [8].

Having in mind all the above mentioned, we expected great differences in electron density distribution between Tl and S and between Pb and S. It is quite obvious that where the first model is concerned (TlS_7^{-13}) the electron density is mainly concentrated between Tl and 4S atoms in the $x-y$ plane and Tl and 2S atoms in the $y-z$ plane, while it is somewhat lower in the vicinity of the S atom located on the z axis. Where the second model is concerned (PbS_7^{-13}) a tendency of the charge to shift towards a part of the cluster that has all the characteristics of a galenite structure is noticed. The two residual S atoms in the $y-z$ plane are in a field of considerably lower electron density. These changes in electron densities are shown in fig. 7 representing the difference in electron densities between TlS_7^{-13} and PbS_7^{-13} clusters in the $y-z$ plane. It is obvious from fig. 7 that the electron density is considerably higher in the vicinity of Pb atoms and is concentrated between Pb, S atoms along the z axis and 4S in the $x-y$ plane (fig. 4). The change in Tl cluster is shifted towards S atoms in the $y-z$ plane (fig. 7) which means that the strength of the chemical bond between Pb and the mentioned 5S atoms is considerably stronger when compared to the strength of the chemical bond with the remaining two S atoms in the $y-z$ plane in the PbS_7^{-13} cluster. This

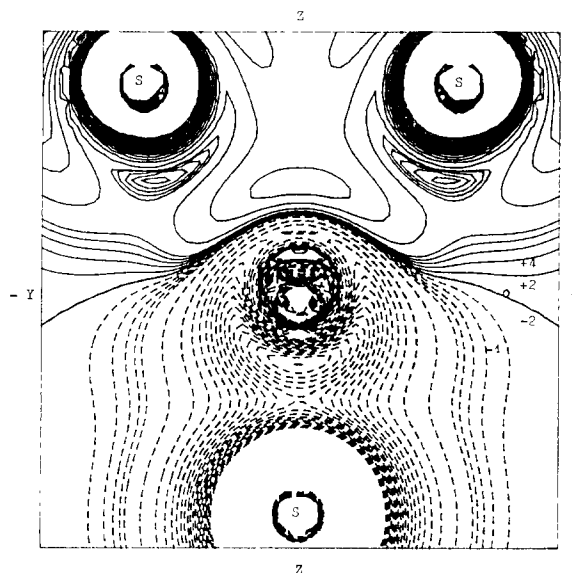


Fig. 7. The difference in electron density between TlS_7^{-13} and PbS_7^{-13} clusters (the dashed line represents negative values).

argument is not valid for the TlS_7 cluster. Therefore, we can expect the presence of Pb in a lorandite lattice to weaken the bond between two neighbouring layers particularly at sites where Pb is built in instead of Tl. The discussion of Balić-Žunić [9] speaks in favour of the results obtained.

The eigenvector values are represented in table 1, from which it is evident that in the case of TlS_7^{-13} the eigenvalue for the highest electronic state is approximately 1.7 eV below the Fermi energy level which is at -1.48 eV, while in the case of PbS_7^{-13} the outer filled electron level lies at the very Fermi energy level (-1.43 eV). Analysing other eigenvalues we found them to be similarly arranged within the energy scale in both

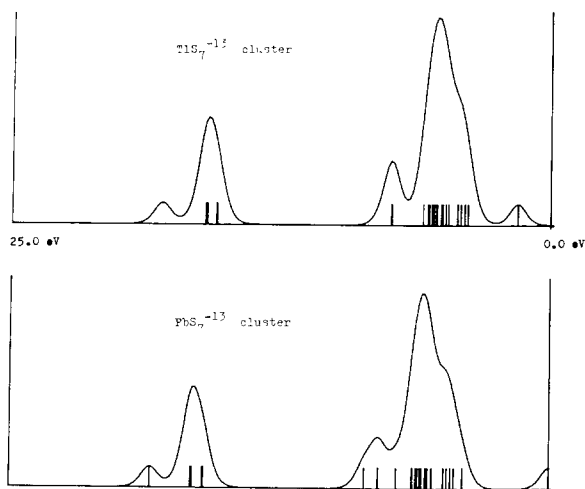


Fig. 8. Plot of the density of states plot.

Table 1
Results of DVM calculations, Eigenvalues and occupation of levels

TlS ₇ ⁻¹³ cluster (system of 58 electrons)			PbS ₇ ⁻¹³ cluster (system of 59 electrons)		
State	Eigenvalue [eV]	Occupation	State	Eigenvalue [eV]	Occupation
1 A1	-17.5493	2	1 A1	-17.5407	2
2 B2	-15.8196	2	2 B2	-15.9229	2
3 B1	-15.8175	2	3 B1	-15.9176	2
4 A1	-15.8028	2	4 A1	-15.9162	2
5 A2	-15.7415	2	5 A2	-15.8427	2
6 A1	-15.3826	2	6 A1	-15.4409	2
7 B2	-15.3518	2	7 B2	-15.4072	2
8 B1	-8.3729	2	8 A1	-8.9465	2
9 B2	-8.3701	2	9 B1	-8.3946	2
10 A1	-8.3363	2	10 B2	-8.3915	2
11 A1	-7.0660	2	11 A1	-7.6726	2
12 A1	-6.8743	2	12 A1	-7.0440	2
13 B1	-6.8047	2	13 B1	-7.0102	2
14 B1	-6.7068	2	14 B2	-6.8828	2
15 B2	-6.6838	2	15 B1	-6.8035	2
16 A2	-6.6168	2	16 A2	-6.7138	2
17 A1	-6.5281	2	17 A1	-6.6740	2
18 B2	-6.4940	2	18 B2	-6.6379	2
19 B2	-6.3361	2	19 B2	-6.4903	2
20 A2	-6.2698	2	20 B1	-6.4355	2
21 B1	-6.2635	2	21 A2	-6.3903	2
22 A1	-6.1351	2	22 A1	-6.2342	2
23 A2	-6.0328	2	23 A2	-6.2105	2
24 B2	-5.6763	2	24 B2	-5.7533	2
25 B1	-5.6522	2	25 B1	-5.7301	2
26 A2	-5.5271	2	26 A2	-5.6080	2
27 A1	-5.3683	2	27 A1	-5.4719	2
28 B2	-5.2400	2	28 B2	-5.3292	2
29 A1	-3.1934	2	29 A1	-4.9735	2
30 A1	-0.4818	0	30 A1	-1.4336	1
31 B1	-0.4608	0	31 B1	-1.2741	0
			32 B2	-0.8316	0

$$E_F = -1.48 \text{ eV}$$

$$E_F = -1.43 \text{ eV}$$

clusters, which was also confirmed by diagrams of the energy density of states (fig. 8). The main differences are observed in the region of the Fermi energy level. Apart from this it should be emphasized that the mentioned diagrams present only molecular orbitals occupied by valence electrons, but not the inner electrons of a metal and sulphur. Another conclusion can be made on the basis of the results presented in table 1 and fig. 8, i.e. that the electron conductivity of lorandite enriched by lead is considerably higher than that of pure lorandite. But this conclusion requires experimental confirmation.

5. Conclusion

On the basis of the performed analysis of a simplified lorandite model, when only a metal and its

nearest neighbours, 7S atoms, are taken into consideration, the assumption can be made that the conversion of Tl into Pb during neutrino capture causes a local distortion of the lattice geometry and consequently destabilizes the lattice.

The mentioned destabilization is expressed in the weakening of the bond between the layers with cubic symmetry particularly at sites where the Pb atoms make a bond with S atoms from the neighbouring layer.

The analysis of electron density enables us to conclude that Pb in a lattice formed of TlS₇⁻¹³ clusters favours a redistribution of electron density that characterizes octahedral symmetry. Apart from a minimum difference of atomic number between Tl and Pb, the electron density is considerably higher near Pb, particularly in the *x-y* plane (fig. 4) thus supporting the fact that the chemical bond is more localized between Pb and S than between Tl and S within the same layer. On

the contrary, the electron density is distributed more diffusely in the case of the TlS₇ cluster. This means that the ion character of the bond between Pb and S is slightly more marked. We can also suppose that a diffusion process of Pb could also be possible under the necessary physico-chemical conditions.

Acknowledgement

The author wishes to thank Dr. Bengt Lindgren from the University of Uppsala for his valuable help and discussions during the preparation of this paper.

References

- [1] M.K. Pavićević, GSI-86-9 report (1986) p. 1.
- [2] J.C. Slater and K.H. Johnson, Phys. Rev. B5 (1972) 844.
- [3] H.L. Skriver, The LMTO method (Springer, Berlin, 1984).
- [4] E.J. Baerends, D.E. Ellis and P. Ros. Chem. Phys. 2 (1973) 41.
- [5] B. Delley and D.E. Ellis, J. Chem. Phys. 76 (1982) 1949.
- [6] B. Lindgren and D.E. Ellis, Phys. Rev. B26 (1982) 636.
- [7] M.E. Fleet, Z. Kristallogr. 138 (1973) 147.
- [8] E. Makovitsky, NATO ASI Series E: Applied Sciences no. 83 (1984) p. 159.
- [9] T. Balić-Žunić and S. Ščavničar, these Proceedings (Int. Conf. on Solar Neutrino Detection with ²⁰⁵Tl, and Related Topics, Dubrovnik 1986) Nucl. Instr. and Meth. A271 (1988) 301.