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Electronic structure and chemical bonding of Li₄Pt₃Si

S.F. Matar^{a,*}, R. Pöttgen^b, A.F. Al Alam^c, N. Ouaini^c

^a CNRS, Université de Bordeaux, ICMCB, 87 Avenue du Docteur Albert Schweitzer, 33600 Pessac, France ^b Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany ^c Université Saint Esprit de Kaslik (USEK), Faculté des Sciences, URA GREVE (CNRS/USEK/UL), Jounieh, Lebanon

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ABSTRACT

The electronic structure of rhombohedral Li₄Pt₃Si (space group R32) is examined from *ab initio* with an assessment of the properties of chemical bonding relating to the presence of different Li and Pt Wyckoff sites. The structure with totally de-intercalated Li keeps the characteristics of the pristine compound with a reduction of the volume albeit with less cohesive energy. The binding energies of Li point to different bonding intensities according to their different Wyckoff sites and indicate the possibility of delithiation. © 2012 Elsevier B.V. All rights reserved.

1. Introduction

In the early stages of research on lithium alloy electrodes, transition metal (*T*) stannides and tin–antimony alloys have intensively been studied [1–3] in order to overcome safety problems (whisker formation causing short circuit) that might occur with metallic lithium as electrode material. Stannides decompose during the lithiation process and form lithium-rich binaries up to Li_{4.4}Sn. Various kinds of tin based composite electrodes have been tested. A main disadvantage of the tin containing electrodes is their high density and following studies consequently focused on silicon based materials. Many binary transition metal silicides have been tested with respect to lithiation and their use as composite electrodes.

In the course of our systematic studies of such intermetallic lithium compounds which might be interesting for battery applications we used the inverse approach. We started detailed phase analytical studies of the Li–*T*–Si systems, determined the crystal structures of new silicides and investigated their potential lithium mobility by solid state NMR spectroscopy. An overview on lithium-transition metal-tetrelides is given in [4]. Although the platinum metal containing silicides will certainly not find application just due to their costs, they are interesting model compounds for studying structure-property relationships. Recent studies showed lithium mobility on the NMR timescale for LiRh₂Si₂ [5], Li₃Rh₄Si₄ [6], and Li₄Pt₃Si [7].

Besides the structural, NMR-spectroscopic and electrochemical characterization, we also started investigations of electronic structure and chemical bonding of such silicides [5,8,9] in the context of first principles calculations within the quantum theoretical density

* Corresponding author. Tel.: +33 5 4000 2690; fax: +33 5 4000 2761.

functional DFT framework [10,11] with an emphasis on potential lithium de-intercalation. Herein we present original results on the energies and the bonding characterizing Li within Li₄Pt₃Si.

2. Crystal chemistry

The structure of Li₄Pt₃Si is presented in Figure 1 and the basic structural data are listed in Table 1. A full discussion of this structure is given in our crystallographic work [7]. Herein we focus only on the crystal chemical features that are relevant for the bonding analyses. The silicon atoms in Li₄Pt₃Si have slightly distorted platinum coordination with Pt-Si distances of 238 and 246 pm, in close agreement with the sum of the covalent radii of 246 pm [12], indicating strong covalent Pt-Si bonding. Always two of such prisms are condensed via common triangular faces, leading to double units Si₂Pt₉ which are condensed via common corners to a three-dimensional network. Within this network one observes a short Pt1-Pt2 distance of 274 pm, comparable to the Pt-Pt distance of 277 pm in face centered cubic platinum [13]. The lithium atoms fill the space left by the network of Pt_{6/2}Si prisms. These larger channels are the favorable structural prerequisite for lithium mobility as was evident from solid state NMR spectroscopy. In the structure we observe only Li-Pt contacts at 257 and 277 pm. Since the silicon atoms are well shaded within the Pt_{6/2}Si prisms there are no Li–Si contacts.

3. Computation methodology

Two computational methods within the DFT were used in a complementary manner. The Vienna *ab initio* simulation package (VASP) code [14] allows geometry optimization and total energy calculations. For this we use the projector augmented wave (PAW) method [15,16], built within the generalized gradient approximation (GGA) scheme following Perdew, Burke and Ernzerhof (PBE) [17]. Also

E-mail addresses: matar@icmcb-bordeaux.cnrs.fr (S.F. Matar), pottgen@uni-muen ster.de (R. Pöttgen), adelalalam@usek.edu.lb (A.F. Al Alam), naimouaini@usek.edu.lb (N. Ouaini).

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Fig. 1. (color online) The crystal structure of Li_4Pt_3Si . Lithium, platinum, and silicon atoms are drawn as medium gray, black, and red circles, respectively. The condensed $SiPt_{6/2}$ trigonal prisms and some relevant interatomic distances in pm are emphasized. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Experimental [7] and calculated (parentheses) structural parameters of Li₄Pt₃Si, space group *R*32 -hexagonal axes-: a = 693.7 (696.8), c = 1627.1 (1646.3) pm, c/a = 2.35 (2.36), V = 0.678 (0.693) nm³.

Atom	Wyck. pos.	x	у	Z
Li1	6 <i>c</i>	0	0	0.725 (0.726)
Li2	18f	0.363 (0.362)	0.932 (0.931)	0.087 (0.086)
Pt1	9e	0.607 (0.608)	0	1/2
Pt2	9d	0.739 (0.736)	0	0
Si	6 <i>c</i>	0	0	0.102 (0.101)

preliminary calculations with local density approximation led to underestimated volumes. The conjugate-gradient algorithm [18] is used in this computational scheme to relax the atoms. The tetrahedron method with Blöchl corrections [16] as well as a Methfessel-Paxton [19] scheme were applied for both geometry relaxation and total energy calculations. Brillouin-zone (BZ) integrals were approximated using the special *k*-point sampling of Monkhorst and Pack scheme allowing equally spaced mesh [20]. The optimization of the structural parameters was performed until the forces on the atoms were less than 0.02 eV/Å and all stress components less than $0.003 \text{ eV}/\text{Å}^3$. The calculations are converged at an energy cut-off of 400 eV for the plane-wave basis set with respect to the k-point integration. A starting mesh of $4 \times 4 \times 4$ is then increased in the successive calculation cycles up to $8 \times 8 \times 8$ for best convergence and relaxation to zero strains. Further in order to include core electrons within the PAW method, use is made of the LAECHG = .TRUE. parameter in the 'INCAR' control file followed by operating a summation of core and valence charge densities using a simple *perl* program [28].

Then all-electron calculations, equally based on the DFT with the GGA-PBE functional [17] were carried out for a full description of the electronic structure and the properties of chemical bonding. They were performed using the full potential scalar-relativistic augmented spherical wave (ASW) method [21,22]. In the ASW method, the wave function is expanded in atom-centered augmented spherical waves, which are Hankel functions and numerical solutions of Schrödinger's equation, respectively, outside and inside the so-called augmentation spheres. In the minimal ASW basis set, we chose the outermost shells to represent the valence states and the matrix elements were constructed using partial waves up to $l_{max} + 1 = 3$ for Pt and Si and $l_{max} + 1 = 2$ for Li. Selfconsistency was achieved when charge transfers and energy changes between two successive cycles were below 10⁻⁸ and 10⁻ ⁶ eV, respectively. The Brillouin zone integrations were performed using the linear tetrahedron method within the irreducible wedge. In order to optimize the basis set, additional augmented spherical waves are placed at carefully selected interstitial sites (IS). Besides the site projected density of states, we discuss qualitatively the pair interactions based on the overlap population analysis with the crystal orbital overlap population (COOP) [23]. In the plots, positive, negative, and zero COOP magnitudes indicate bonding, antibonding, and non-bonding interactions, respectively.

4. Results and discussion

4.1. Geometry optimization, cohesive energies and charge analysis

Table 1 provides the experimental and calculated crystal structure parameters. The geometry optimized lattice parameters and atomic positions are found in good agreement with the experimental data [7]. The larger volume is due to the use of the GGA which is over-estimating lattice spacing. An agreement is also found for the shortest distances (in pm): Li1–Li2 = 256; Li1–Pt2 = 277; Li2– Pt1 = 257; Pt1–Si = 240. In order to examine the effect of lithium de-intercalation, additional calculations were performed assuming a full Li de-intercalation leading to 'Pt₃Si' composition as well as selective departures of Li1 and Li2.

The full geometry relaxation keeps the trigonal structure within space group R32 of pristine ternary Li₄Pt₃Si. *V*(Pt₃Si) = 0.417 nm³ is 0.276 nm³ smaller and the difference is due to the departure of 24 Li (*Z* = 6), i.e. 0.0115 nm³ per Li. This is slightly smaller than the atomic volume of ~0.013 nm³. The difference is likely due to ionized Li in Li₄Pt₃Si. In such a hypothesis it becomes important to check the stability of Pt₃Si against a potential decomposition into the elements. For this purpose the energies of the constituents are calculated: E(Pt) = -6.09 eV; E(Si) = -5.42 eV and E(Li) = -1.909 eV. With $E(Pt_3Si) = -24.75 \text{ eV}$ per formula unit (FU), $\Delta E = -24.75 \text{ eV} + 3 \times 6.09 \text{ eV} + 5.42 \text{ eV} = -1.06 \text{ eV}$, i.e. in spite of the large volume change, the resulting compound is stable with respect to the atomic constituents.

It is also interesting to note that Pt_3Si with monoclinic C2/m structure [24] has a total energy of -24.95 eV. This makes its cohesive energy larger (-1.26 eV) with respect to R32 de-lithiated Pt_3Si which is then qualified as a metastable compound if a full departure of Li is operated.

The cohesive energy (enthalpy) of Li_4Pt_3Si obtained by subtracting the energies of Li, Pt and Si with respecting their stoichiometries, amounts to -9.51 eV, i.e. almost nine times larger than de-lithiated compound. This translates a destabilization of the compound when Li is fully removed.

Then one can estimate the average lithium binding energy:

 $E(\text{Li}_4\text{Pt}_3\text{Si}) = -37.02 \text{ eV/FU}$ resulting in $E_{\text{bind.}} = -4.634$ for 4 Li, i.e. -1.159 eV/Li. Removing selectively Li1/Li2 results in: $E_{\text{bind.}}(\text{Li1}) = -1.471 \text{ eV}$ and $E_{\text{bind.}}(\text{Li2}) = -1.357 \text{ eV}$. The absolute values correspond to the energy needed to remove Li. At first inspection, one may deduce that a random departure of Li might be energetically favored. However, the lower average binding energy of -1.159 eV when compared to the binding energies of the specific Li crystallographic sites just reflects the fact that binding energies of Li atoms will be different depending on the composition and structure. In fact a truly random (de)lithiation could be expected in a fully ideal situation of binding energies which are constant and independent of Li content and Li atomic arrangement. That would, for the present case, then lead to the equal binding energies for all three cases (binding energies for the two Li positions and average binding energy). Then a stepwise de-intercalation should be favored with less bonded lithium (Li2) departing first.

The calculated energies involved with the removal of lithium out of Li₄Pt₃Si are in the range of ~ -1 to -1.5 eV. They correspond, with inverse sign, to the average intercalation voltage, *V*. These values are close to the LiYSi value of -1.691 eV [9] and intermediate between the highest intercalation voltages for archetype Li intercalation compounds LiMO₂ (*M* = 3*d* transition metal) [25] and Li_xSi binaries with ~ 0.30 V [26].

We further analyze the charge density issued from the self consistent calculations using the AIM (atoms in Molecules theory) approach [27] developed by Bader who devised an intuitive way of dividing molecules into atoms as based purely on the electronic charge density. Typically in chemical systems, the charge density reaches a minimum between atoms and this is a natural region to separate atoms from each other. Such an analysis can be useful when trends of charge transfers are examined; however they do not constitute a tool for evaluating absolute ionizations. The computed charge changes ΔQ results are such as:

Li1: +0.974; Li2: +0.945; Pt1: -1.367; Pt2: -1.461; Si:+0.433. Neutrality is obtained upon applying the stoichiometry 6 Li1, 18 Li2, 9 Pt1, 9 Pt2, 6 Si (Li₂₄ Pt₁₈Si₆ or 4 Li₆Pt₃Si formula units). It can be noted that the ionic character of Li is slightly different for the two sites and Li1 is more ionic than Li2; this can be connected with different mobility of Li at the two sites and bonding characteristics discussed below. Also Pt behaves differently according to the lattice site with a larger negative character on Pt2. These features should be further illustrated by a detailed analysis of the site projected electronic density of states and the bonding between the constituents.

4.2. Electronic structure and chemical bonding

In as far as the optimized lattice parameters are in good agreement with experiment we use the latter (Table 1) to analyze the

Pt1-Si

Pt2-Si

Pt1-Pt2



Fig. 2. (color online) Site projected density-of-states (PDOS) for Li₄Pt₃Si (top) and the lithium free homologue (bottom).



Fig. 3. (color online) Pt–Si and Pt–Pt bonding in Li₄Pt₃Si (top) and the lithium free homologue (bottom).

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electronic structure and the chemical bonding with all electrons full potential ASW method. The site projected density of states (PDOS) for both Li₄Pt₃Si and 'Pt₃Si' are shown in Figure 2. In both panels there is a small intensity but finite density of states (DOS) at the top of the valence band (VB) so that the compound is metallic and the zero energy along the *x*-axis is with respect to the Fermi level ($E_{\rm F}$). The character of the conduction is nevertheless different: In $Li_4Pt_3Si E_F$ crosses itinerant s like states formed by all chemical constituents while in the lithium-free (hypothetic) compound $E_{\rm F}$ crosses the upper part of the Pt *d* states at higher intensity. These largely filled d states are found centered around -3 eV within the VB in the ternary compound (upper panel) due to the four electrons surplus arising from the four lithium atoms while they are centered at -2 eV in 'Pt₃Si'. Platinum belonging to the two independent Wyckoff sites form different PDOS shapes but show similar line shapes around the lower part of the VB, i.e. in the energy region where they mix with Si p states. This is also shown around -10 eV with the Si s like states. However the chemical bonding is expected to involve directional orbitals such as *p* and *d* rather than non directional orbitals as s like ones. This is detailed below.

Figure 3 shows the COOP for Li_4Pt_3Si and Pt_3Si in two panels accounting for Pt1, Pt2 and Si with their site multiplicities (cf. Table 1). For both Pt1–Si and Pt2–Si bonds the whole range of the VB is of bonding character (positive COOP), in spite of the antibonding



Fig. 4. (color online) Bonding for Li with Pt and Si in Li_4Pt_3Si (top) and the integrated COOP for Li1 and Li2 with platinum (bottom).

negative COOP just below E_F ; which show larger intensity in the Li free compound. On the contrary Pt1–Pt2 bonding is of less intensity in Li₄Pt₃Si in both its bonding (positive) and antibonding (negative) COOP than in Pt₃Si whose antibonding COOP's extend above E_F . This translates the lower cohesive energy calculated above and results from the large diminishing of the volume calculated above, whereby bonding is enhanced due to smaller interatomic separations and larger intensity interactions.

The bonding of Li with Pt and Si within the VB is detailed in Figure 4. The upper panel shows the COOP for atom-to-atom interactions for the sake of comparing relative intensities. Clearly Li-Pt bonding is dominating over Li-Si. This follows from the prismatic environment of Si with Pt1 and Pt2 while Li are capping the rectangular faces of the prism. The different Li-Pt intensities follow mainly from the course of the distances, ex. the highest COOP for Li2–Pt1 corresponds with d(Li2-Pt1) = 257 pm while lower intensity Li1–Pt2 COOP is relative to a larger separation of 277 pm. The relative strength of the bonding of Li1 versus Li2 with Pt in Li₄Pt₃Si can be further shown using the integrated COOP: iCOOP. iCOOP is unit-less and translates the trend: the larger the area below the curve, the larger the bonding. This is plotted in the lower panel of Figure 4. Clearly the Li1-Pt bonding intensity is larger than Li2-Pt one and this result illustrates further the binding energies differentiating Li1 from Li2 and favoring a larger binding for the former.

5. Conclusion

Lithium rich Li₄Pt₃Si is metallic with itinerant like electrons crossing the Fermi level. From full geometry optimizations, the structure with totally de-intercalated Li keeps the characteristics of the pristine compound with smaller volume and less cohesive energy. Lithium shows different binding energies along the two Li Wyckoff sites in agreement with chemical bonding analysis. A step wise de-intercaltion is energetically favored. The calculated energies involved with the removal of lithium out of Li₄Pt₃Si { -1 to -1.5 eV}, are close to LiYSi and intermediate between the highest intercalation voltages for LiMO₂ and Li_xSi binaries.

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