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First-principles calculations for Li insertion into InSb

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Abstract

First-principles calculations are presented for the zinc-blende structure compound InSb, a candidate anode material for Li batteries. The atomic structure of InSb during Li insertion is discussed in the light of local density functional theory calculations based on plane-wave pseudopotential and linear muffin tin orbital methods. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electrochemical potentials a few hundred MeV above that of Li metal would be desirable in an anode material, from the standpoint of operating safety. Since carbon-based anodes [1], which have electrochemical potentials for Li similar to Li metal, are otherwise favorable because their open structures readily accommodate Li, it seems worthwhile to investigate the suitability of non-carbon-bearing channeled structures. This contribution focuses on the zinc-blende structure compound InSb [2], which may be viewed as channeled, although it is strongly bonded in three dimensions.

First-principles calculations based on local-density-functional theory are presented for the properties of Li in InSb and related materials. Experimental investigations [2–4] of the structural evolution of InSb during electrochemical cycling are still incomplete, and we therefore focus here only on the first discharge cycle, for which the broad outlines of the structural transformations are known.

2. Method

We refer to the compositions that arise during electrochemical cycling of InSb as $Li_{x+y}In_{1-y}Sb$. In this formula, x represents the amount of interstitial and y the amount of substitutional Li in the zinc-blende InSb framework structure. We consider both In- and Sb-coordinated tetrahedral interstices, denoted by T_{In} and T_{Sb}, respectively [5], for Li interstitials in InSb. It would be desirable to treat small non-zero values of x and y, in view of the trace solubilities typical of Li in semiconductors, but the smallest value of x treated is 1/8.

We employ the plane-wave pseudo-potential (PWP) method [6] in most of the calculations. Pseudopotentials were generated with the Troullier-Martins code, with the In and Sb 4d shells treated as valence electrons, and with a basis set cut-off energy of 80 Ry. To complement the PWP method, calculations have also been performed with the full-potential-linear-muffin-tin orbital (FLMTO) method [7], which yields highly precise results, but is restricted for computational reasons to smaller unit cells. Most of our calculations employed either the primitive unit cell (1 formula unit) or the conventional cubic unit cell (4 formula units). The equilibrium lattice constants predicted in our PWP and FLMTO calculations both differed by less than 1% from the experimental value, 6.47 Å, consistent with previous work [8,9].

The limit $x = 2$, $y = 1$ corresponds to the compound Li_3Sb, in which both T_{Sb} and T_{In} interstitial sites are occupied, and Li is substituted on the In sublattice of the zinc blende structure. Our PWP calculations yield an equilibrium lattice parameter of 6.35 Å, about 3% lower than the experimental value.

3. Results and discussion

A marked difference is observed between the electrochemical potential curves in the first discharge cycle and in

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subsequent cycles [2]. Apparently, the first discharge cycle serves to ''condition'' the electrode, after which relatively stable cycling behavior is established. From a phenomenological point of view, several types of structural changes come into consideration when Li is introduced into InSb.

3.1. Lithium insertion into InSb

Our calculations indicate that the T_{Sb} sites are the preferred locations for Li in pristine InSb. (Some preliminary calculations [10] had suggested that the sites T_{In} might be favored for small x. Our more complete results, however, indicate that T_{Sb} is energetically preferred at all values of x).

One anticipates that only a relatively small amount of Li can be accommodated interstitially, in thermodynamic equilibrium. Interpolating between the FLMTO calculations for $x = 0$ and 1, we find that the approximate lattice constant expansion per unit Li concentration is

$$\frac{\Delta a}{a\,\Delta x} \sim 0.05$$

It has been observed empirically [11] that crystal lattices of compounds tend to amorphize when the lattice constant expands (as a result, for example, of hydrogenation or irradiation) by only about 1%. Applied to lithiated InSb, this criterion would correspond approximately to $x_{amorp} = 0.2$, which is small compared with the full extent of the discharge [2], $x_{max} \sim 2$–3. There is no experimental evidence [2], however, of Li-induced amorphization.

3.2. Lithium substitution: compensation

It may be favorable thermodynamically (although the precise kinetic path is unclear) to substitute a fraction of Li atoms on the In sublattice. A special case is the ''line of compensation'', $x = 2y$, for which one-third of the Li atoms occupy substitutional sites. The electrons donated by interstitial Li atoms are then exactly compensated by Li acceptors on the In sublattice. Compensation may be favorable thermodynamically because bonding states are essentially filled, and antibonding states are essentially empty. Kinetic barriers to In diffusion, however, may prevent Li substitution from occurring, at relatively small x, in the absence of preexisting In vacancies.

3.3. Formation of $Li_{3-\delta}In_{\delta}Sb$

A reaction to form the compound Li_3Sb, by extruding In metal during the insertion of Li, is considered. This reaction most likely limits the thermodynamic solubility of Li in InSb, as do analogous reactions in other zinc-blende compounds [12]. Our calculations predict an electrochemical potential for this reaction of 0.9 eV, relative to Li metal. Measured first-discharge potentials [3,4], on the other hand, show a plateau at 0.75 eV for ball-milled specimens and 0.6 eV for single crystals. The results of extended X-ray absorption fine structure (EXAFS) measurements [4] suggest that the plateau is associated with the displacement of In from its sublattice in the zinc blende structure. Although local density functional theory calculations typically underestimate electrochemical potentials for Li batteries, our predicted voltage in this case is higher than experiment. The theoretical prediction corresponds to the ideal reaction $(1/3)(3Li + InSb \rightarrow Li_3Sb + In)$ in which the extruded component forms metallic In in its tetragonal crystal structure. The formation of metallic In, however, requires mass transport, and the measured electrochemical potential may correspond to the local displacement of In to a transient site within the InSb matrix, before the extrusion takes place.

4. Summary

We have explored with local density functional theory some structures that arise when Li is inserted into zinc-blende InSb. The calculations predict that Li occupies the T_{Sb} sites initially. We are unable to make a precise prediction of the solubility limit of Li in the framework lattice, but it is thought to be small. When this limit is exceeded, we believe that the extrusion of In occurs, with the formation of a ternary system with composition $Li_{3-\delta}In_{\delta}Sb$, similar to Li_3Sb. The extruded In eventually crystallizes in its usual metallic form, but this process may be delayed by the mass transport required for the In to reach the specimen surface or internal pores.

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