

Pressure-Sensitive Modeling of the Reversible Lithiation of Vacant Thiospinel $(\text{In}_{0.5}\square_{0.5})[\text{In}_{1.5}\text{Sn}_{0.5}]\text{S}_4$

J.-P. Connerade,^{*,1} J.-C. Jumas,[†] and J. Olivier-Fourcade[†]

^{*}The Blakett Laboratory, Imperial College, London SW72BZ, United Kingdom; and [†]Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR 5072 CNRS, CC 015, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

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A simple atomic model is described in which lithiation appears as a reversible pressure acting on confined atomic species which constitute the host material. It is demonstrated, by *ab initio* calculations of the properties of a confined atom as a function of the cavity radius, that the ionization of Sn occurs in the manner which has been observed, i.e., it passes directly from Sn^{IV} to Sn^{II} without the appearance of Sn^{III} . This is shown not to be the case for a confined atom with no *d* shell present, and therefore we conclude that the observed property is of atomic origin and is directly related to the high compressibility of *d* orbitals. Extensions of our model are suggested to include relativistic effects, which would enable *ab initio* calculations of the Mössbauer signals to be attempted for the lithiated compounds. This would provide an independent test of our model. © 2000 Academic Press

BACKGROUND

Recently, it has been shown by Elidrissi Moubtassim *et al.* (6) that a particularly simple example of topotactic insertion occurs for Li^+ in the ternary vacant spinel-type structure of $(\text{In}_{0.5}\square_{0.5})[\text{In}_{1.5}\text{Sn}_{0.5}]\text{S}_4$ ($\square = \text{vacancy}$). Crystal structure determinations carried out by Adenis *et al.* (7) from X-ray diffraction on single crystal in the *Fd3m* space group and quantitative chemical analysis led to the following extended formula: $(\text{In}_4\square_4)_{8a}[\text{In}_{12}\text{Sn}_4]_{16d}(\text{S}_{32})_{32c}$. Lithium insertion was performed by the chemical route via *n*-butyllithium or by electrochemical methods. NMR on ^7Li (6) has demonstrated that lithium was Li^+ and the double-line subspectra have been related to two types of lithium site with different mobilities (tetrahedral and octahedral sites). It was found experimentally that (i) the active change induced by insertion in this material is a reduction of Sn from Sn^{IV} to Sn^{II} as evidenced by Mössbauer spectroscopy (ii) there is no change in the overall crystal structure, as evidenced by X-ray diffraction and (iii) a model based on a rigid band structure cannot explain the changes (8) because it would imply a progressive reduction for all Sn atoms, whereas Mössbauer spectra show rather clearly that only some Sn atoms are reduced, i.e., that the effect is a local one, close to the sites where lithiation actually takes place. For certain compounds, one also finds that (iv) neutral Sn can also occur for instance in another thiospinel $\text{Cu}_2\text{FeSn}_3\text{S}_8$ (9) or $\alpha\text{-SnO}$ (10).

In order to keep matters as simple as possible, it is obviously desirable to use a compound that contains only Sn^{IV} and no Sn^{II} before lithiation, so that the appearance of Sn^{II} in the Mössbauer spectra can unambiguously be correlated with the insertion of lithium ions. A suitable material turns out to be $\text{In}_{16}\text{Sn}_4\text{S}_{32}$, which has a pure Sn^{IV} resonance. Upon lithiation of this material, a key experimental fact emerges, namely, that reduction takes place from Sn^{IV} to Sn^{II} directly, without any evidence for the formation of any intermediate Sn^{III} . This reduction has been clearly observed by Mössbauer spectroscopy of ^{119}Sn (Fig. 1) (1)

INTRODUCTION

The development of electrode materials for reversible batteries is a subject of considerable topical interest, with numerous potential applications (1, 2). Of particular importance are those which involve the insertion of lithium ions in a solid host, usually chosen as a complex material with an open spinel-type structure through which the ions can migrate before insertion (3–5).

For the process to be reversible, it is important that it should not involve discontinuous phase transitions, such as those that arise when the lattice structure changes. The most favorable situations are thus expected to involve isomorphic changes, known to electrochemists as *topotactic* insertion of ions. There are two aspects to the quest for suitable materials. The first is the search for the “best” electrode, while the second is the desire to understand, in terms of a simple model, the processes by which reversible insertion can occur. This involves seeking the simplest examples, so that basic ideas can be tested. The present paper concentrates on this second scheme.

¹ To whom correspondence should be addressed.



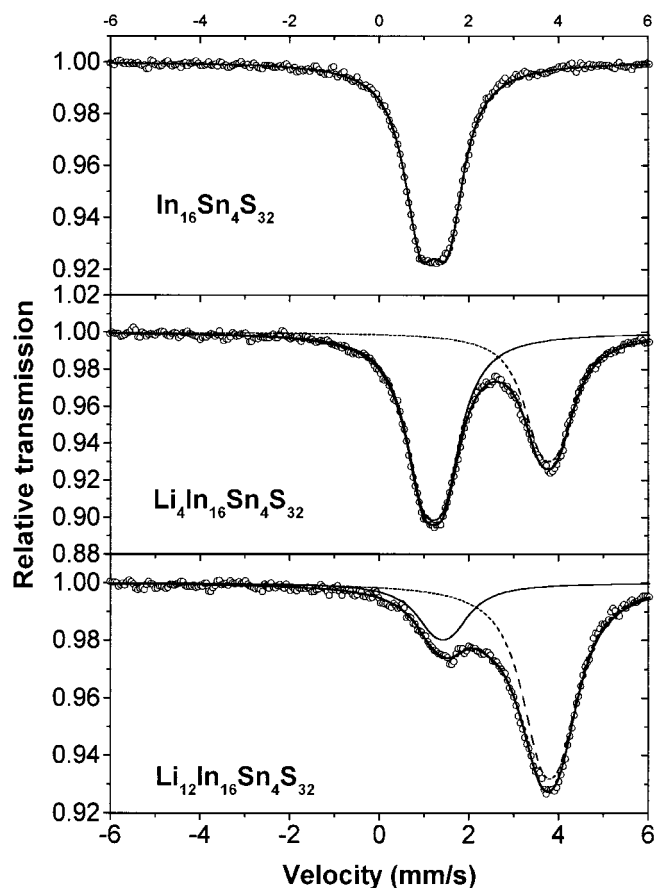


FIG. 1. ^{119}Sn Mössbauer spectra recorded at 77 K for $\text{In}_{16}\text{Sn}_4\text{S}_{32}$ before and after lithium insertion.

which shows for the pristine compound $\text{In}_{16}\text{Sn}_4\text{S}_{32}$ one split line (isomer shift ≈ 1.2 mm/s, quadrupole splitting ≈ 0.6 mm/s) characteristic of Sn^{IV} in a slightly distorted octahedral site. After lithium insertion, an evident reduction of Sn^{IV} to Sn^{II} takes place and the spectrum shows a second subspectrum with hyperfine parameters (isomer shift ≈ 3.7 mm/s, quadrupole splitting ≈ 0.4 mm/s) characteristic of Sn^{II} . The relative contribution of the Sn^{II} subspectrum increases linearly when the lithium content increases.

DISCUSSION

The thrust of the present paper is to demonstrate that most of these features can be incorporated into a very simple quasi-atomic model, leaving aside the more complex structural aspects of the problem, and that this model also allows reversibility to emerge as a natural consequence of the mechanism proposed. The principal assumptions of the model we are using have already been presented in a number of earlier papers, for example in (11) and again in (12). In brief, the point is that a pressure-induced distortion of atomic wavefunctions can be calculated *ab initio* by

confining the atom within an impenetrable spherical cavity, and making use of the energy change as a function of the volume change to determine a quantum compressibility. When defining the potential change at the walls of the cavity, self-consistent field calculations turn out to be most stable if the wavefunction falls to zero over a few mesh points of the grid, which is achieved by introducing a potential step of finite rather than infinite height. This also allows one to check that the result is independent of the nature of the confining step by raising the step height until there is no further change in the binding energy. In practice, a good value to use is about 5 atomic units (one atomic unit = 27.2 eV). Our basic argument is that reversible insertion proceeds by a local (polaronic) deformation of the lattice which arises by dilating or compressing the structure so as to accommodate the inserted ion. Pressure effects (13) and “effective pressure” arguments have often been invoked in the discussion of impurities in solids (14), and a simple argument for computing pressures from atomic volume changes has been suggested (15). A more refined approach (11, 12) is the model originally introduced by Michels *et al.* (16) and Sommerfeld and Welker (17) who showed that ionization, or the formation of the conduction band in a solid, can be understood in a very simple way by considering a hydrogen atom confined in a spherical cavity. Confined atoms have recently become of renewed interest (18–21), and it has been demonstrated that many-electron atoms from the transition sequences present some quite remarkable properties in cavities (22, 23).

To illustrate our argument, we show, in Fig. 2, the properties of the Sn atom and its first few ions in a spherical cavity, plotted as a function of the cavity radius. Each one of the points on the graphs is one full self-consistent field calculation according to the model proposed by J. P Connerade (11) with no adjustable parameters. Absolute energies are plotted on the ordinate.

The calculations demonstrate that:

(i) in a cavity of radius smaller than about 2.3 a.u. the only stable ground state is Sn^{IV} , i.e., that Sn^{I} , Sn^{II} , and Sn^{III} have lost their outer electrons;

(ii) in a cavity of larger radius, the stable ground state ion is Sn^{II} , with an almost negligible chance of forming Sn^{III} for a very narrow range of cavity radii close to the point labeled X in the figure. Thus, one has a natural way of understanding why the reduction proceeds directly from Sn^{IV} to Sn^{II} without an intermediate stage of Sn^{III} . This turns out to be an essentially atomic effect;

(iii) lithiation can thus be represented as an increase in cavity radius across the figure, which is the direction of reduction or of decreasing ionization, because the Li atoms act as electron donors;

(iv) Sn^{II} is the stable ground state over a restricted range of cavity radii between X and Y in the figure, beyond which neutral Sn has the lowest energy ground state.

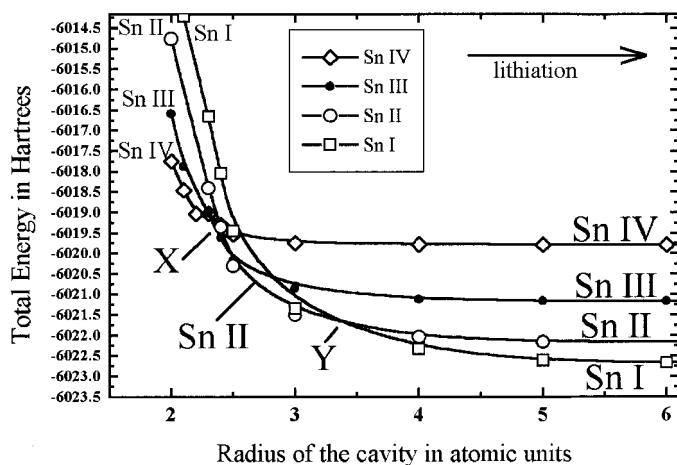


FIG. 2. Calculation of the ground state of the first few Sn ions placed in a cavity, as a function of cavity radius. Notice the existence of two crossing points, labeled X and Y in the figure. To the right of Y, the ground state is Sn^I. Between X and Y, it is Sn^{II}, and to the left of X, it is Sn^{IV}. Thus, Sn^{III} does not appear as a viable ground state, except possibly in a very narrow range near point X (see text).

Thus, the confined atom scheme incorporates the known facts about the appearance of the different forms of Sn without any need for sophisticated crystal structure calculations. It has the further advantage that it yields wavefunctions directly in the different regimes and that, from these wavefunctions, a number of other observables can be computed.

In order to demonstrate that this effect is specific to Sn atoms, we have performed the exact same calculation for a homologous element, namely, Mg, which has a $3s^2$ rather than a $5s^2$ outer subshell. In Fig. 3, we show the corresponding data. The essential difference between Figs. 2 and 3 lies in the positions of the crossing points between the curves, as a result of which Mg^{III} is the ground state of confined Mg over quite a wide range of radii below 3 atomic units, whereas Sn^{III} does not occur as the ground state of confined Sn over any appreciable range.

Notice that this conclusion is arrived at by purely ab initio calculations, without the introduction of any adjustable parameters. It thus emerges as a purely atomic property due to the radial compressibilities of the atomic wavefunctions. The reason for the difference in behavior between Sn and Mg can readily be understood. Indeed, there has been a great deal of study of the differences in atomic compressibility which arise through the presence of d electrons, as a consequence of the Mayer–Fermi theory of orbital collapse (12), and these phenomena are well-documented in atomic physics (24). Neutral Sn is characterized by a subvalence d shell, which, in common with all outermost filled d subshells, is highly compressible or “soft.” When the atom is compressed, it acquires more and more

d character, and the crossing points are very close to each other.

For magnesium, on the other hand, because there is no subvalent d shell, but only a compact and rather rigid $2p^6$ shell, the Mg^{III} and Mg^{IV} ions are very small and relatively incompressible. Indeed, it is necessary to reduce the cavity radius to around 2.5 a.u. before clear distortion of the $2p$ wavefunctions begins to appear.

An alternative to the confined atom model which retains all the essential features of the atomic approach is to vary the effective nuclear charge. In a sense, it can be considered as a complementary picture. In the confined atom scheme, the perturbation is entirely external to the atom, while in the effective charge model, the perturbation is entirely internal. Consequently, these models set upper and lower bounds for the influence of otherwise equivalent perturbations on an atomic system. The confined atom model has the advantage that it can be related directly to an equivalent pressure because the atom occupies a definite volume, changes in which can be related to change in the total energy.

Mössbauer spectroscopy is the main diagnostic tool for the lithiated system. The main conclusions from the experiment are (i) that the intermediate situation (lithiated) does not correspond to Sn^{III}, but to an inhomogeneous mixture of Sn^{II} and Sn^{IV} (25) (ii) that the Sn^{IV} ions are characterized by a Mössbauer shift of about 1.15 mm/s and an effective charge of 1.18–1.25 s electrons (26) (iii) that the Sn^{II} ions have a Mössbauer shift of 3.5 mm/s and an effective charge of 1.92 mm/s (26). This means that, in effect, lithiation must produce a charge transfer of about 0.7 $5s$ electrons for the transition from Sn^{IV} to Sn^{II} to occur (iv) the Sn^{IV} ions are located in octahedral sites, whereas the Sn^{II} can occupy various sites in the lattice. The octahedral sites are charac-

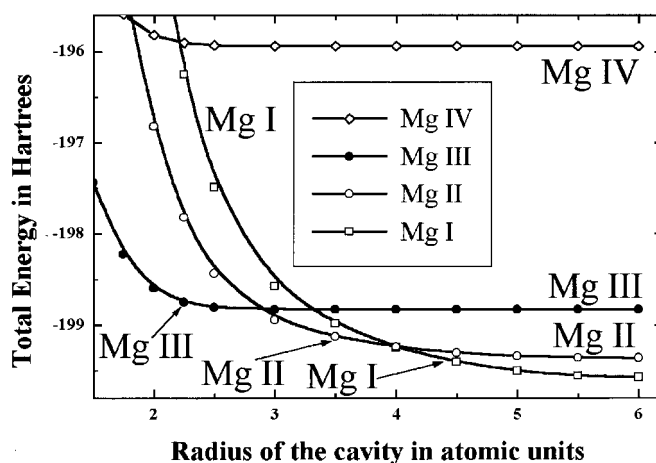


FIG. 3. Ground state energies for the lowest levels of the first few ions of Mg in a cavity, as a function of the radius of the cavity. Notice how the crossing points differ considerably from those of Fig. 2 and, in particular, that, below a cavity radius of about 3 atomic units, the ground state becomes Mg^{III}.

terized by interatomic spacings of about 2.6 Å, while larger sites are available for Sn^{II}. Thus, the process of lithiation, in which the number of Sn^{II} ions increases, can be considered as an increase in the cavity radius for atoms lying close to lithium ions. We find that the Mössbauer peak for Sn^{II} grows linearly with the amount of Li inserted in the lattice.

Furthermore, experimental information is available from NMR spectroscopy which confirms that lithium is not inserted in the metallic form but rather as ions and that there are generally two available sites for insertion in these ternary compounds (25).

From the standpoint of the confined atom model, we do not need to consider an actual charge transfer in order to compute the Mössbauer shift. This shift actually depends on the density ρ_s of *s*-symmetric charge near the nucleus, which is of course modified as the atomic wavefunctions respond to the influence of the external cavity on the atom. Thus, the Mössbauer shift for an atom in a cavity depends on the radius of that cavity. Since the inner 1*s* wavefunctions are dominant in the computation of the density, and since they are of very small radius, the shift is very small for a given electronic configuration. However, when there is a discontinuous change of ground state (from Sn^{IV} to Sn^{II}) as a result of the effects described above, the Mössbauer shift undergoes considerable change, and the ratio of the two shifts can be calculated and compared with experiment.

In addition, we can consider the broadening of the Mössbauer lines. The natural width of the Mössbauer transition is very small indeed (about 10^{-7} – 10^{-8} eV for Sn in a solid). However, when lithiation occurs, the lines are broadened, because there is a distribution of Sn atoms at different distances from an inserted Li ion. To estimate this broadening, we can set upper and lower bounds for the existence of stable Sn^{IV} and Sn^{II} ions, because they can only “live” in cavities with a certain range of sizes. We thus have *s* wavefunctions from the extreme cavity sizes and, from the total *s* densities, we can calculate the maximum broadening of the Mössbauer transitions resulting from lithiation.

In principle, the confined atom model is suitable for the computation of Mössbauer shifts. However, there is an important limitation of our present model. The Hartree–Fock scheme we use is nonrelativistic, whereas the properties of atomic wavefunctions near the edge of the nucleus (where the Mössbauer signature is determined) are dominated by relativistic effects.

To treat this, it will therefore necessary to extend the model for confined atoms to the Dirac–Fock scheme, in

order to achieve a coherent interpretation of the data, relating the changes in the atomic wavefunctions we have described to the changes in the Mössbauer spectrum resulting from lithiation.

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