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Lithium Ion Electrode Materials and the Properties of Atomic Orbitals

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The properties of suitable materials for electrodes of lithium-ion rechargeable batteries are discussed. The key to understanding the insertion process is the localization of the ionic and electronic charge distribution in the lattice. A suitable sequence of spinel materials has been selected and investigated experimentally using a variety of techniques. The resulting observations are discussed in terms of an atomic model based on comparisons with known spectra and on *ab initio* Hartree–Fock calculations. © 1999 Academic Press

INTRODUCTION

Electrode materials for the new generation of batteries are made from materials into which the reversible insertion and removal of an element in ionic form (i.e., $Li \rightarrow Li^+$ for Lithium-ion batteries) can occur. For this to be possible, the host lattice must be able to accept both the ion and its associated electronic charge. Much of the information on appropriate lattices is empirical. Beyond this, however, one wishes to understand the underlying physical processes and to develop simple models for them. At the level of its atomic arrangement, the host lattice must possess enough vacant sites to capture a certain number of ions and a sufficiently open structure to allow their diffusion through the solid, but the structure must also be sufficiently stable to allow such changes to take place reversibly.

At the level of synthesis or preparation of the material, soft chemistry (1, 3) is regarded as the most appropriate technique, as it favors the formation of metastable phases through nonreconstructive (i.e., displacive) phase transformations with change of composition. Such transformations are ideal for preserving the topotacticity and reversibility of the reaction. Intercalation or deintercalation reactions by either chemical or electrochemical paths belong to these methods of synthesis. During the insertion process, the materials must accept one or more electrons coming from the inserted atoms. If one excludes the case of complete delocalization, which does not even allow an electron to be associated with a given atom (fully metallic limit), the additional electrons will modify the oxidation state of a certain number of ions, and this, in general, leads to the creation of a mixed valence compound. The atom or atoms forming the host lattice must be able to change their shape and especially their volume in order to allow these local distortions to occur within the solid. The classification of mixed valence compounds proposed by Robin and Day (4) is based on electron–atom exchanges within a given lattice. It results from the competition between a localization parameter which describes the polarizing effect of an electron on its environment, and consequently a deformation of the initial site (vibronic coupling), and an interaction parameter involving two sites hosting the same element, which allows delocalization to occur (via a transfer integral)

One can thus distinguish between three classes of materials:

1. *Class I.* The effect of the deformation of the lattice is large, the sites are chemically very different, and there is no delocalization.
2. *Class II.* The influence of electronic transfer between sites and electronic polarization of an atom in an individual site are comparable. The electron remains localized on a single site, but thermal or optical delocalization by transfer between similar sites is possible (transitions in electrochromic materials).
3. *Class III.* The system is intrinsically delocalized, and the sites are not crystallographically distinct from each other. There is no influence of lattice deformation. The observation of two oxidation states of the element depends on the specific time scale of the spectroscopic technique used relative to the intrinsic time scale of electronic transfer. It will also depend on the type of transfer, i.e., whether it is direct between sites or proceeds via ligand.

Electronic transfer between sites is therefore an important factor which determines the nature of the material and its associated properties (5–7). Electronic transfer also plays a dominant role in determining the Redox properties of lithium-ion electrode materials. We believe that the same

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type of behavior, well characterized for molecular complexes, occurs quite generally in solids, with further complexity due to the existence of a lattice of different dimensionality.

Two broad classes of behavior have been characterized (8):

(a) *Type I.* The element inserted in the lattice is in the ionic state, and the electron concerned can either be localized on a site (Classes I and II) or delocalized in a band usually made up from the *d* orbitals of a transition element (Class III). The notion of localization then depends somewhat on the speed of the transfer between sites and on the method of observation (4). Such are the majority of cathode materials.

(b) *Type II.* The element inserted in the lattice retains metallic in character, with a significant delocalization of its electrons. This is the case for anode materials with highly covalent (C_6Li) or metallic (LiAl) host lattices.

The current goal is to seek out anode materials whose properties would be close to Type II, but for reasons of safety and reversibility, lithium should be stored inside the lattice in its ionic form, as in Type I materials. Thus, one really seeks materials intermediate between Type I and Type II. We have therefore concentrated on the study of different insertion mechanisms which can arise in strongly covalent host materials, our approach being to analyze the nature and atomic origin of electronic transfer. One hopes thereby to achieve a better understanding of the electrochemical properties (such as charge capacity, potentials, and reversibility). We have selected the spinel structure, which has the advantage of a large number of empty sites available for lithium ion insertion, with the possible occurrence of mixed valence and vacancies (9). The constituent atoms of the lattice are from the *p* sequence, which guarantees strong covalence. Often, it is advantageous to introduce a transition element, because of the additional flexibility this introduces in the wavefunctions, as will be described below.

BACKGROUND

We have devoted particular attention to compounds involving tin. Indeed, a Japanese research group has reported particularly promising performance for anode materials based on oxides of tin (10), although the results of Ref. (10) and the redox mechanism proposed have both been questioned by other researchers (11, 12). Thus, compounds involving Sn emerge as particularly interesting.

The Spinel Host

The spinel structure is generally represented by the chemical formula AB_2X_4 in the cubic space group $Fd\bar{3}m$. In a compact cubic stacking of anions X, the cations A and B occupy, respectively, one-eighth of the available tetrahedral sites (sites 8*a*) and one-half of the available octahedral sites (sites 16*d*). These two types of site can be more or less vacant, and their distribution can become partly or totally inverted, according to the formula (13)

$$(A_{1-\lambda}B_\lambda)_{\mathrm{Td}}[A_\lambda B_{2-\lambda}]_{\mathrm{Oh}}X_4, \quad \text{where } 0 \le \lambda \le 1.$$

Such an arrangement leaves many vacant sites (both of tetrahedral 8*b* and 48*f* and of octahedral 16*c* type) and is therefore a very favorable host structure for lithium insertion [14]. To this should be added the facts (a) that a spinel structure is open in three dimensions (i.e., is not layered), which confers greater rigidity to the material under lithium insertion than for layered materials, because it expands in three dimensions, and (b) that lithium ions have high mobility throughout the lattice.

When x lithium atoms are inserted, $x\mathrm{Li}^+ + x$ electrons are introduced into the lattice. To analyze the consequences of this insertion and relate them to observed properties, two factors must therefore be considered: (1) where the lithium ions localized? and (2) how are the electrons absorbed? To shed some light on both of these questions, we have chosen to study a sequence of model compounds whose structure is derived from the spinel indium sulfide In_2S_3, whose unit cell is represented by the formula $(In_{5,66}\square_{2,33})[In_{16}]S_{32}$, with an unoccupied tetrahedral site $\square$ and a fully occupied octahedral site. Solid solutions based on this structure were achieved by substituting In with Sn, Cu, Mn, Fe, Co, and Ni in order to generate the following families: $(In,\square)_8[In,Sn]_{16}S_{32}$, $(In,Cu)_8[In]_{16}S_{32}$; $(In,Fe)_8[In,Fe]_{16}S_{32}$; and $(Cu)_8[M,Sn]_{16}S_{32}$, with M = Mn, Fe, Co, Ni.

Where Does the Lithium Go?

High-resolution NMR studies of ^7Li (Fig. 1) show that, in all cases, the inserted lithium is always in its cationic form Li^+ with two different environments. Indeed with increasing number of inserted lithium, the lines do not present (Fig. 1A) any significant differences of chemical shift and are characteristic of ionic lithium Li^+. All spectra consist of two superposed lines (Fig. 1B) with a thin Lorentzian profile for the first and a Gaussian for the second, both centered around slightly different frequencies. This NMR spectra structure indicates that the lithium ions have two different environments with the presence of tetrahedral and octahedral vacant sites within the spinel structure. Since the line width is directly related to the motion, the thin component has been attributed to a large mobility type of lithium (octahedral) while the other corresponds to a less mobile one (tetrahedral) (15).

Where Do The Electrons Go?

In the main, two cases have been found. Either (i) the inserted electrons modify the charge of B and its state of

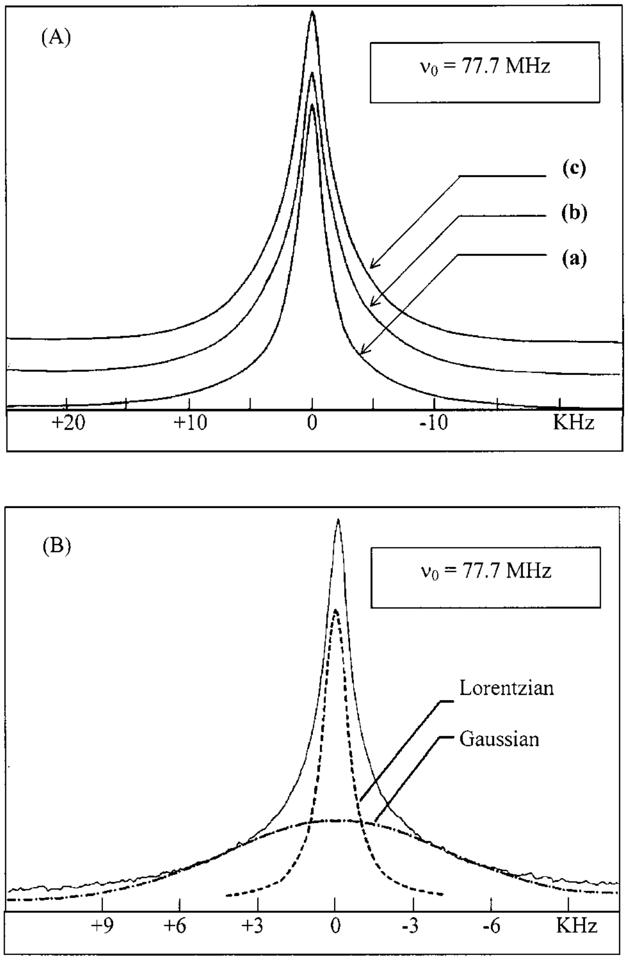

FIG. 1. ^{7}Li NMR from (15); (A) experimental spectra: (a) $Li_{1.26}In_{16}Sn_4S_{32}$, (b) $Li_{1.54}In_{16}Sn_4S_{32}$, and (c) $Li_{2.94}In_{16}Sn_4S_{32}$; (B) central line simulation.

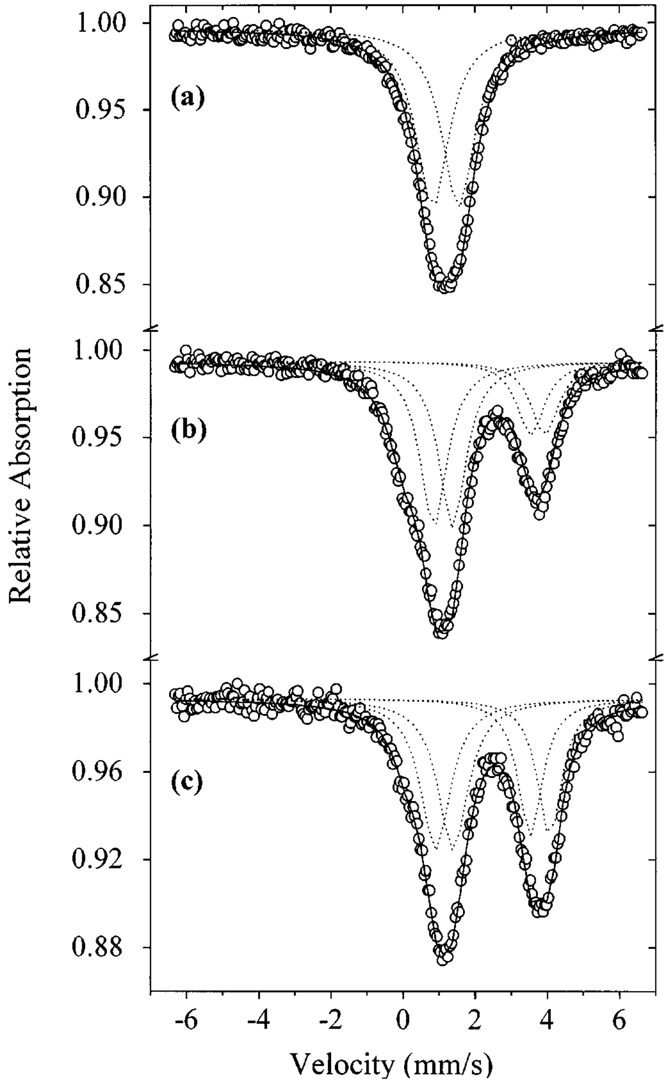

FIG. 2. ^{119}Sn Mössbauer spectra: (a) $In_{16}Sn_4S_{32}$, (b) $Li_{6.24}In_{16}Sn_4S_{32}$, and (c) $Li_{8.36}In_{16}Sn_4S_{32}$ from (15).

oxidation or (ii) they alter the charge of all the elements, without any change of oxidation.

(i) *Electrons localized on B.* This case arises for $(In,\square)_8[In,Sn]_{16}S_{32}$, in which the Sn atom is reduced according to the relation $Sn^{4+} + 2e \rightarrow Sn^{2+}$. This reduction has been observed by Mössbauer spectroscopy of ^{119}Sn (Fig. 2) (16, 17), which shows for the pristine compound $(In,\square)_8[In,Sn]_{16}S_{32}$ one split-line (Fig. 2a) with hyperfine parameters (isomer shift ~1.2 mm/s, quadrupole splitting ~0.6 mm/s) characteristic of Sn^{IV} in a little-distorted octahedral site. After lithium insertion, an evident reduction of Sn^{IV} to Sn^{II} takes place since the spectra (Figs. 2b and 2c) show 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^{IV} subspectrum decreases linearly when the lithium content increases. This mechanism has been quantified by a close-coupling calculation (18). In this situation, the lattice is only slightly distorted, with a weak increase in the lattice spacing. One does not observe any reconstructive phase transition and insertion is topotactic (Fig. 3). The change of oxidation state of Sn affects only some atoms. This leads to the coexistence of two states (Sn^{4+} and Sn^{2+}) for the same species on the same octahedral site. Calculations (19) show that the lithium ion behaves like a point defect, creating a localized state inside the gap. For this state to be sufficiently deep and stable, one site out of two occupied by the lithium ions must be tetrahedral. X-ray absorption and photoemission spectroscopy do not reveal significant changes in the conduction or valence bands.

(ii) *Electrons distributed in the lattice.* This situation arises in the other cases, all of which involve a transition element, in which case there is a greater flexibility of

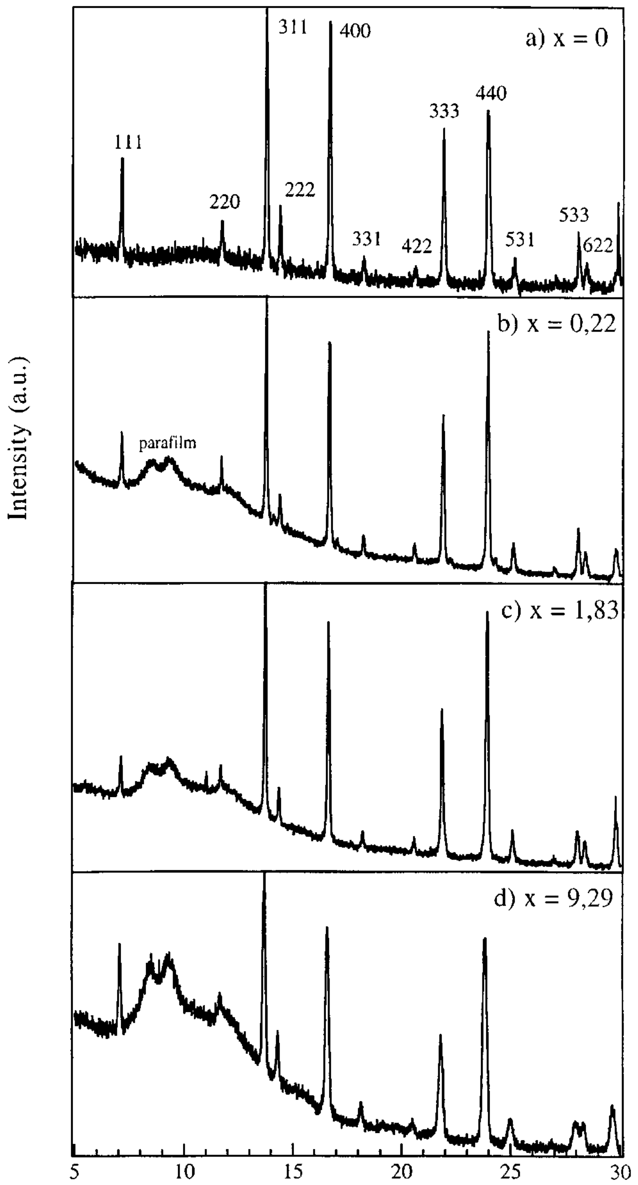

FIG. 3. X-ray diffraction spectra (Cu$K\alpha$) for $Li_xIn_{16}Sn_4S_{32}$ ($x = 0$, 0.22, 1.83, and 9.29).

wavefunctions (to be described below) and the atomic polarizability allows electrons to be distributed over the lattice with no change in the oxidation state. Thus, the electrons merely change the partial charge state of the elements, but do not formally alter their state of oxidation. There can, however, be an evolution in the nature of the bonds.

Several cases arise:

(a) An increase in covalence by migration of metallic elements from octahedral to tetrahedral sites (20), transitions from spin-up to spin-down (21), and formation of covalent bonds Li–S (22) can occur. These cases occur for $(In, Fe)_8[In, Fe]_{16}S_{32}$, in which the migration of Fe atoms from octahedral to tetrahedral sites is clearly demonstrated by Mössbauer spectroscopy on ^{57}Fe (Fig. 4). For $Li_{0.7}In_{16}Fe_8S_{32}$ (Fig. 4a) the ^{57}Fe Mössbauer spectrum consists of two subspectra corresponding, respectively, to the 16*d* site (quadrupole splitting ~3.2 mm/s) and 8*a* site (quadrupole splitting ~0.9 mm/s) of the spinel structure. With the increasing lithium content, one (Fig. 4b) then two (Figs. 4c and 4d) additional subspectra, which have been attributed, respectively, to the tetrahedral 8*b* sites (quadrupole splitting ~0.7 mm/s) and octahedral 16*c* sites (quadrupole splitting ~2.6 mm/s), appear. This Fe migration is confirmed by a Rietveld analysis (23). For $(Cu)_8[Fe, Sn]_{16}S_{32}$, a change in the spin state of Fe is observed. This situation leads to a deformation of the lattice, with a slight contraction of the lattice spacing, which results in an amorphization of the material.

(b) An increase in ionicity due to migration of the metallic elements from the tetrahedral to octahedral sites with an increase in the charge state of the sulphur atoms can occur. This situation occurs for $(In, Cu)_8[In]_{16}S_{32}$. The migration of In atoms from tetrahedral to octahedral sites is brought

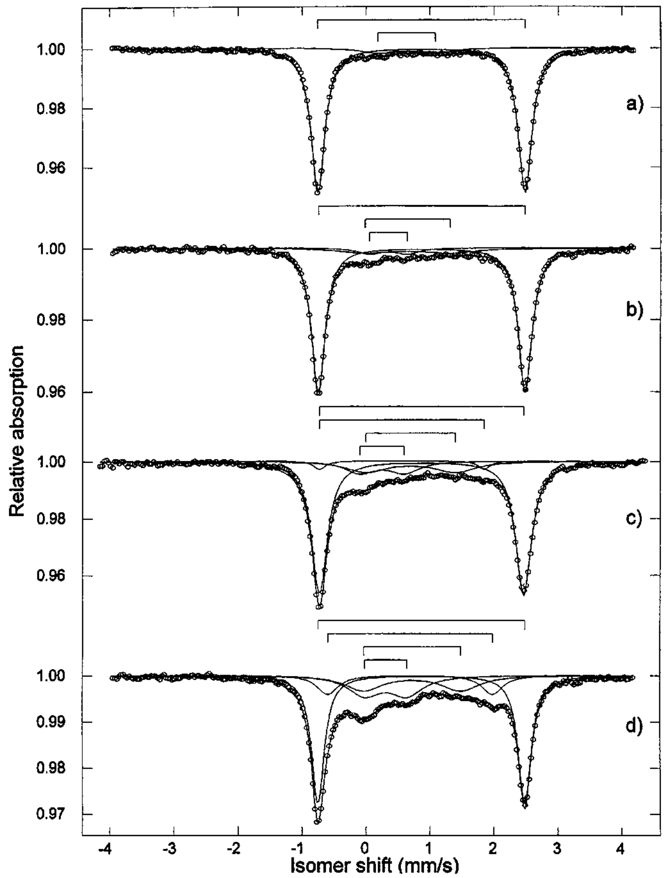

FIG. 4. ^{57}Fe Mössbauer spectra of the lithiated phases $Li_xIn_{16}Fe_8S_{32}$: (a) $x = 0.7$, (b) $x = 5.2$, (c) $x = 12.2$, and (d) $x = 16.4$ from (20).

out by a Rietveld analysis (24) and the increase in the charge state of sulphur is seen by X-ray photoabsorption spectroscopy (22) at the K edge of sulphur. In this case, the lattice is not much distorted and the quantity of lithium inserted can be large.

DISCUSSION

Insertion of lithium takes place more easily and with a smaller perturbation of physical properties if the electrons become localized on individual atoms by changing their oxidation state. Some elements are more likely to favor this type of change. For example, note the difference between two nearby elements in the Periodic Table, viz. indium ($Z = 49$) and tin ($Z = 50$). The first modifies the electron distribution in its bonds, whereas the second prefers to change its oxidation state. Since the structure and chemistry of the compounds involved are in all cases rather similar, it is interesting to consider whether there is any clue in the atomic spectra of free In and Sn atoms, which could shed some light on these differences of behavior.

At several stages in the discussion above, we have noted that transition elements have properties that can modify the insertion properties of a host compound very markedly. This is readily understood in terms of the Mayer–Fermi model of orbital collapse (25), because *d* orbitals experience an effective potential, which results from a balance between centrifugal and electrostatic potentials, as a result of which they are more sensitive to their environment than, for example, *s* or *p* orbitals. This sensitivity is greatest when *d* orbitals are actually being filled, that is to say in the transition sequence, where atoms become highly compressible and may change the effective radius of their *d* electrons quite dramatically according to their excitation state (26) or their environment (27). On the other hand, once orbital collapse has occurred, i.e., the *d* subshell is filled, it becomes progressively more rigid as other electrons are added around it to form heavier elements in the Periodic Table.

The addition of a transition element in the composition of the host thus allows the elementary cell as a whole to respond to changes in lithiation without internal reorganization, merely by exploiting the flexibility in the *d* wavefunctions of the transition metal, and so this situation favors the distribution of the extra charge over the whole cell, rather than its attachment to an individual atom. The fact that spin transitions are found for Fe is consistent with the involvement of the *d* electrons (responsible for the magnetism of this element) in the readjustments that arise from lithiation. The case of Cu is also an interesting one. Although this element has a filled *d* subshell and one external *s* electron, its properties in the bulk are not determined solely by the *s* electron, but involve the *d* electron as well. This is well known from the properties of the sequence of conductors copper, silver, and gold. If their conducting properties were (as elementary theory suggests) entirely due to the external *s* electrons, then they would all be of the same color. The reason their colors differ is due to the different properties of the *d* electrons (28) and this difference is also revealed by their atomic absorption spectra. The presence of Cu in the composition of the host material leads to a similar situation to the presence of transition metals.

Turning now to Sn, we have a rather different situation, because the $4d^{10}$ electrons in Sn are screened from the environment by a closed subshell $5s^2$ and two $5p$ electrons. Since Sn lies very close to In in the Periodic Table, and since both are present in the host, there is now a competition of behavior between these two elements to decide what will actually occur. In In, the $4d^{10}$ subshell is filled and screened from the environment by a closed $5s^2$ subshell, while there is only one $5p$ electron. Thus, the $4d^{10}$ subshell is quite rigid in both of these elements and rather hard to distort. The option of distorting the $4d$ subshell to distribute the charge by polarizational attachment to the whole unit cell does not exist. In the case of In, if we refer to the atomic energy level diagram (Fig. 5), which we obtain by *ab initio* Hartree–Fock calculations, we see that it would actually be more difficult in terms of energy to doubly ionize In than to break the $4d$ subshell open. In Sn, on the other hand, it is easier to doubly ionize the atom by removing both *p* electrons than to break the $4d$ shell open. Thus, the cross over in behavior between whether it is more advantageous to ionise the atom twice or to break the $4d$ shell open occurs between In and Sn. This is a direct measure of the rigidity of the *d* electronic shell versus valence electrons and gives a strong hint as to why the behavior for Sn is markedly different from that for In. Experimentally (for free atoms), it is known that the position of the double-ionization threshold relative to the inner-shell excitation spectrum has a very marked effect on the photoabsorption spectrum for elements near In and Ga because of a similar crossover (29). The outermost *d*-shell spectra differ completely between In and Sn for free atoms for precisely this reason (30, 31).

The analogy may be taken yet further by considering how the atoms In and Sn respond in calculations in which a Hartree–Fock atom is contained within an impenetrable sphere whose boundary conditions simulate to some extent the influence of a confining lattice (32). What is found in this case (see Fig. 6a and 6b) is that the cross over between double-ionization and inner-shell ionization referred to above is very sensitive to the presence of the cavity. There is a direct relationship between cavity radius and the pressure applied to the atom. Similarly, lithiation leads to a change in the lattice pressure experienced by the host atoms, and one can thus deduce that the behavior of the crossing point is altered. Note that either positive or negative pressure can be applied in this model by reversing the sign of the potential step at the wall of the cavity.

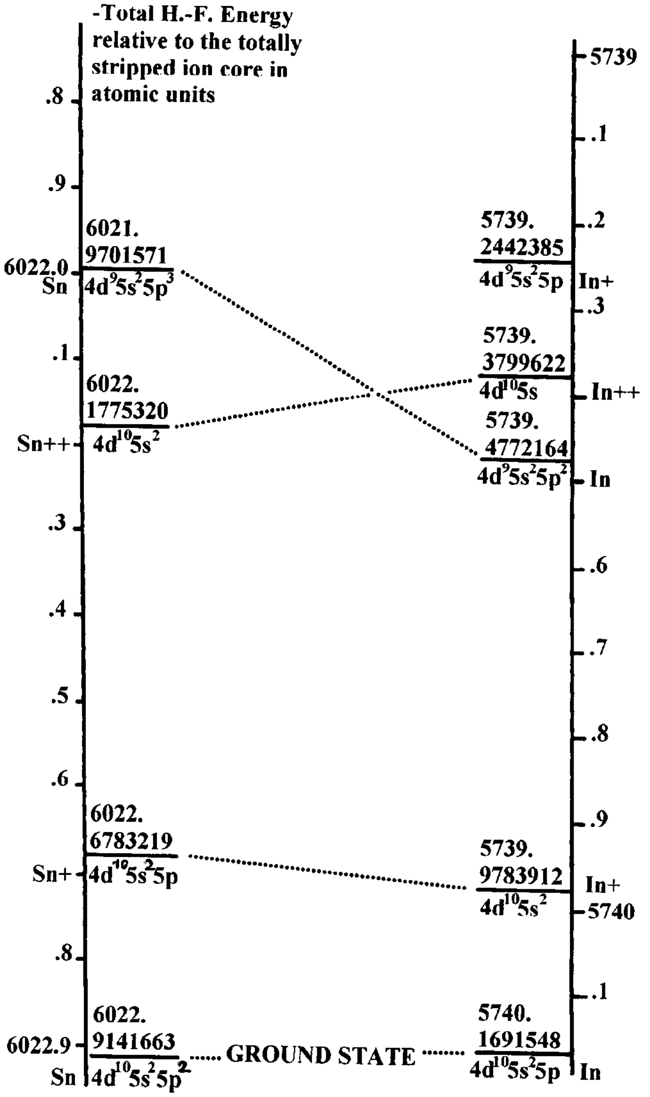

FIG. 5. Atomic energy level diagram for Sn and In obtained from Hartree–Fock *ab initio* calculations. The energy scales are shown with the ground states of the neutral atoms aligned, and absolute energies are shown above each of the levels. Note the crossover between the doubly ionized states and the inner-shell excited states of the neutral, which occurs between Sn and In, and which is responsible for differences in spectral behavior between these atoms.

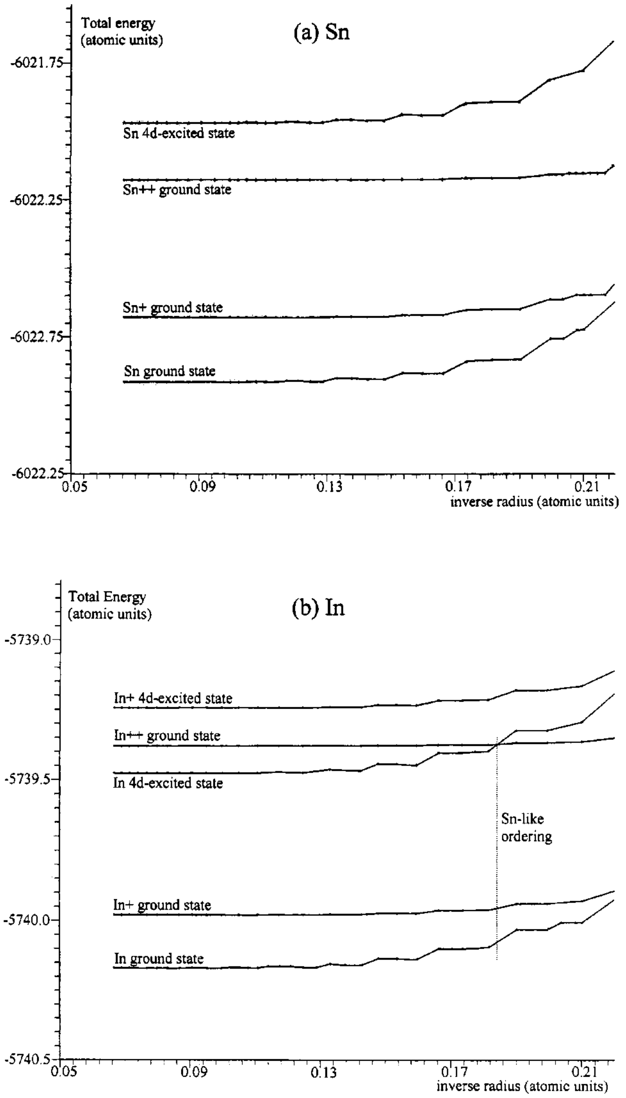

FIG. 6. Evolution of the atomic energy levels of (a) Sn and (b) In placed inside a spherical cavity, as a function of the inverse radius. The left-hand side of the plot tends to the free atom limit, which is the same as in the previous figure. On the right-hand side, one sees the evolution of the configurations as the cavity is made smaller. For plot (b), notice the crossing between the double ionization limit and the doubly excited state of the neutral. To the right of this crossing, the order of the levels in In becomes the same as it would be for Sn, whereas for Sn under the same conditions the ordering is unaltered. Thus, the crossover between In and Sn orderings is a sensitive function of the cavity radius. Each point on the plot corresponds to the one converged self-consistent field calculation.

CONCLUSION

The observations suggest that lithiation and the associated changes in the host lattice are considerably affected by the participation of *d* electrons from the metallic elements present in the host material. If the *d* shell is readily deformable, as occurs for Cu and for transition elements, then the electronic charge associated with the inserted ion becomes distributed over the whole unit cell. If, on the other hand, no transition element is present, but the metal involved is Sn, then the electronic charge becomes more localized on Sn, which changes its oxidation state. These differences of behavior can be understood in terms of fundamental properties of the atoms themselves and in particular of the rigidity of the *d* electronic shell, which can be deduced by performing *ab initio* calculations for the free atom and for atoms confined within a spherical cavity.

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