



## STABILITY OF FULLERENE-BASED SYSTEMS

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**Abstract**—Chemical modification of fullerenes such as the  $C_{60}$  molecule is a promising way to generate novel materials with tailored properties. Exohedral insertion of atoms in the interstitial sites of the  $C_{60}$  solid has created a new class of superconductors. Encapsulation of atoms in the fullerene cage is expected to lead to stable  $M@C_{60}$  endohedral complexes with a very interesting optical response. We study the stability of  $M_xC_{60}$  solids and  $M@C_{60}$  molecules using a Born–Haber cycle. Our analysis not only provides the formation energies, but also elucidates the stability trends across the periodic table.

**Keywords:**  $C_{60}$ ,  $C_{60}$ -endohedral complexes of,  $C_{60}$ -intercalation compounds of formation enthalpy, superconductivity.

### 1. INTRODUCTION

The successful synthesis of the  $C_{60}$  “buckyball” molecule [1] in bulk quantities [2] has opened a way to create modified fullerenes, either free molecules [3] or solids, with tailored properties. An important discovery in this respect was that of superconductivity at high temperatures in the alkali intercalated  $C_{60}$  solid [4, 5]. The following intensive research activity in the field of chemically modified fullerenes, specifically solid  $C_{60}$  intercalation compounds and  $C_{60}$  molecules containing encapsulated atoms, has been reviewed in [6, 7]. The key to a successful synthesis of novel compounds is their thermodynamic stability. In the following, we show how to estimate this quantity for both solid  $C_{60}$  intercalation compounds and free  $C_{60}$  based charge transfer complexes containing encapsulated atoms.

Formation energy, which is intimately related to the thermodynamic stability, is hard to calculate precisely, since cohesion in these ionic systems is dominated by a large Coulomb or Madelung energy [8]. The difficulty to obtain reliable data for the formation energy is best documented by the scarcity of *ab initio* values for the intercalated  $C_{60}$  solid [9, 10] and endohedral complexes of  $C_{60}$  [11] alike. Since in particular in the solids the published values for the formation energies differ by up to 5 eV [9, 10], we decided to determine the formation energy in an alternative way. Our approach is to decompose the formation process of modified fullerenes into physically well-defined steps, and to combine these steps

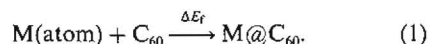
into a thermodynamic Born–Haber cycle [12–14]. This procedure not only provides formation energies for the systems of interest, but also explains stability trends across the periodic table.

### 2. BORN–HABER CYCLE

In this section, we review the derivation of the Born–Haber cycles which are used to determine the stability of free  $M@C_{60}$  endohedral complexes and of bulk  $M_xC_{60}$  intercalation compounds. This approach can also be applied to multicomponent intercalation compounds, but this rather simple extension will not be discussed here.

#### (A) Endohedral $M@C_{60}$ complexes

Let us first consider the formation of the free  $M@C_{60}$  endohedral complex from the free atom  $M$  and the isolated  $C_{60}$  molecule. The corresponding formation energy  $\Delta E_f$  is defined by



If  $\Delta E_f$  is negative, the complex  $M@C_{60}$  is stable against decomposition into the pure components, namely  $M(\text{atom})$  and free  $C_{60}$ . We determine  $\Delta E_f$  by formally decomposing the formation process of  $M@C_{60}$  into several physically well-defined steps and evaluating the energies involved in the individual steps. This procedure, known as the Born–Haber cycle, has been described in [14]. The cycle for the formation of  $M@C_{60}$  is illustrated in Fig. 1.

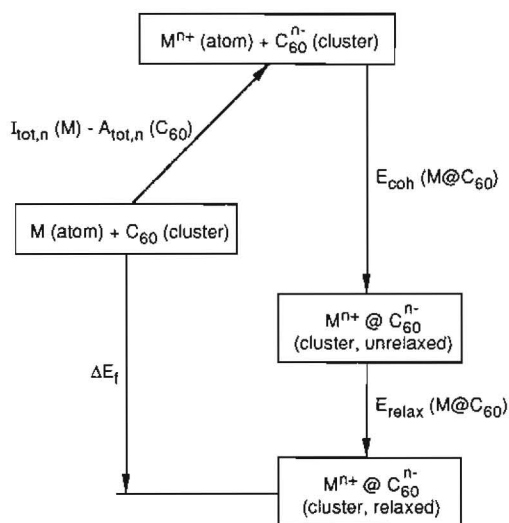


Fig. 1. Born–Haber cycle used to predict the formation energy  $\Delta E_f$  of donor  $M@C_{60}$  endohedral complexes. (From [14], © Elsevier Science Publishers.)

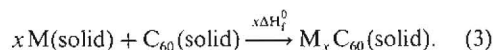
This cycle has been constructed based on the assumption of a closed-shell electronic configuration for  $M$  leading to an ionic  $M-C_{60}$  bond, which is supported by *ab initio* calculations for stable  $M@C_{60}$  complexes [11, 15]. Based on this Born–Haber cycle, the formation energy  $\Delta E_f(M^{n+}@C_{60}^{n-})$  can be obtained as

$$\Delta E_f(M^{n+}@C_{60}^{n-}) = I_{\text{tot},n}(M) - A_{\text{tot},n}(C_{60}) - E_{\text{coh}}(M^{n+}@C_{60}^{n-}) - E_{\text{relax}}(M^{n+}@C_{60}^{n-}). \quad (2)$$

In the first step of the cycle, corresponding to the first energy term on the right-hand side, we consider the ( $n$ -fold) ionization of the  $M$  atom and transfer of this charge to the  $C_{60}$  molecule. This step requires the total ionization energy of the  $M$  atom,  $I_{\text{tot},n}(M)$ , and the total electron affinity of  $C_{60}$ ,  $A_{\text{tot},n}(C_{60})$ . In the next step, the system gains a considerable amount of energy  $E_{\text{coh}}(M^{n+}@C_{60}^{n-})$ , dominated by a Coulomb attraction, when the ion  $M^{n+}$  is moved from infinity into the center of the negatively charged  $C_{60}$  cage. This energy gain must be corrected for the energy needed to cross the dipole layer on the  $C_{60}^{n-}$  cage, and for non-ionic (e.g. closed-shell interatomic repulsion)  $M-C_{60}$  interactions. In the last step of the cycle, the  $M^{n+}$  ion is allowed to move off-center inside  $C_{60}^{n-}$ , releasing the polarization energy  $E_{\text{relax}}(M^{n+}@C_{60}^{n-})$  of the cage. This Born–Haber cycle can be trivially modified for the case of an endohedral charge transfer complex  $M^{n-}@C_{60}^{n+}$ , formed by the electron *acceptor* element  $M$ . More details about the energies involved in the individual steps are given in [14].

### (B) Solid $M_xC_{60}$ compounds

A similar formalism can be used to determine the formation enthalpies  $\Delta H_f^\circ(M_xC_{60})$  of solid intercalation compounds of  $C_{60}$  [12, 13]. The formation enthalpy of  $M_xC_{60}$  from bulk  $M$  and  $C_{60}$  at  $T = 0$  K is defined by



For a donor compound,  $\Delta H_f^\circ(M_xC_{60})$  can be estimated using the Born–Haber cycle analogous to that shown in Fig. 1, as

$$x\Delta H_f^\circ = xE_{\text{coh}}(M) + E_{\text{coh}}(C_{60}) + xI_{\text{tot},n}(M) - A_{\text{tot},n}(C_{60}) - E_{\text{coh}}(M_x^{n+}C_{60}^{n-}). \quad (4)$$

Again, this Born–Haber cycle is derived based on the assumption of a purely ionic bond between the intercalants  $M$  and the  $C_{60}$  solid [9, 10]. In the first step of the cycle, the  $M$  and the  $C_{60}$  solids are separated into atoms and molecules, respectively. The energy involved in this step is the cohesive energy of  $M$ ,  $x E_{\text{coh}}(M)$  (note that  $xM$  atoms occur in the formula unit of  $M_xC_{60}$ ) and binding energy of a  $C_{60}$  molecule in  $C_{60}$  (solid),  $E_{\text{coh}}(C_{60} \text{ solid})$ . In the next step, the  $M$  atoms are  $n$ -fold ionized, requiring the total ionization energy  $I_{\text{tot},n}(M)$ . The charge is transferred to the  $C_{60}$  molecule, yielding  $A_{\text{tot},n}(C_{60})$ . In the last step, the  $M^+$  and  $C_{60}^{n-}$  ions are combined to form the solid. The formation energy  $E_{\text{coh}}(M_x^{n+}C_{60}^{n-})$ , which is released in this step, is dominated by the Madelung energy of the crystal. Again, this Born–Haber cycle can be trivially modified for the case of an intercalation compound  $M_x^{n-}C_{60}^{n+}$ , formed by the electron *acceptor* element  $M$ . More details about the energies involved in the individual steps are given in [12, 13].

### 3. DISCUSSION OF THE RESULTS

We used the Born–Haber cycle to determine the stability of potentially interesting  $M_xC_{60}$  intercalation compounds and  $M@C_{60}$  endohedral complexes. The numerical values for the formation energies and enthalpies have been given in [12–14]. These predictions are in good general agreement with experimentally determined stabilities of  $M_xC_{60}$  compounds ( $M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) [16] and the ease to synthesize free  $M@C_{60}$  molecules. In the following, we concentrate on distinguishing likely candidates for intercalation in the periodic system, and an analysis of stability trends.

In Fig. 2, we present a schematic summary of our results for the stability of  $M_xC_{60}$  solids and  $M@C_{60}$  molecules. Since the formation enthalpies and energies can vary dramatically when changing the concentration  $x$  of  $M$  in the solid or the oxidation state of

(a) Solid  $M_x C_{60}$

(b)  $M@C_{60}$  molecules

Fig. 2. View of the periodic table with elements M considered as intercalants in (a) solid  $M_x C_{60}$  compounds and (b) free  $M@C_{60}$  endohedral complexes. Elements which do form stable systems in exohedral processes defined in eqns (1) and (3) are indicated by a dotted hatched background. Elements which do not form stable systems are shown on a grey background.

M, we only include results for the most stable systems in Fig. 2. Our results indicate that in general donor elements of groups IA and IIA of the periodic system, as well as early rare earths, form stable compounds, while acceptor elements of groups VIA and VIIA do not form stable compounds. This general trend holds for both the  $M_x C_{60}$  solids and the  $M@C_{60}$  molecules.

These results can be interpreted as resulting from several trends across the periodic table. The heats of formation are dominated by the electrostatic cohesion (Madelung or Coulomb energy) of the ionic system on the right-hand side of the Born–Haber cycle which, for a given group, does not change significantly from element to element. Also, the cohesive energies of the different elements in the periodic table in their condensed state, which occur in the Born–Haber cycle for  $M_x C_{60}$ , and the relaxation energies, which enter in the Born–Haber cycle for  $M@C_{60}$ , do not change significantly across the periodic system. More important are the changes of the ionization potentials and electron affinities which

occur on the left-hand side of the Born–Haber cycle, shown in Fig. 1. Indeed, element-specific differences in the energetics of this ionization step explain the stability of donor-based  $C_{60}$  intercalation systems and the lack of stability for acceptor-based  $M_x C_{60}$  compounds, indicated in Fig. 2.

This latter trend can be illustrated by comparing the energetics of the ionization step incurred during the formation of  $K_3 C_{60}$  and a hypothetical solid  $Cl_3 C_{60}$ . The energy invested to ionize three K atoms per formula unit,  $3I(K) = 13.02$  eV, is comparable to the energy gained by attaching one electron each to the three Cl atoms per formula unit,  $-3A(Cl) = -10.85$  eV. Yet the energy gained in the  $C_{60}$  molecule in the donor system,  $-A_{tot}(C_{60}^{3-}) = -1.09$  eV, is much smaller than the energy invested to triply ionize  $C_{60}$  in the acceptor system,  $I_{tot}(C_{60}^{3+}) = 34.96$  eV. Hence the total energy cost of the ionization step for the K-based donor system,  $\Delta E(\Delta Q) = 11.93$  eV, is much smaller than the energy cost for the Cl-based acceptor system,  $\Delta E(\Delta Q) = 24.11$  eV. As can be seen in Fig. 1, lowering the energy cost of the ionization step makes the final state more stable. Consequently, donor-based compounds are expected to be much more stable than acceptor compounds. In the present case, taking into

account also the energetics of the other steps, we find  $K_3 C_{60}$  to be stable with  $\Delta H_f^\circ = -2.09$  eV and  $Cl_3 C_{60}$  to be unstable with  $\Delta H_f^\circ = +3.29$  eV.

In order to understand the more detailed stability trends within a group or series in the periodic system, we investigate the energetics of the adduct cohesion and ionization steps in the Born–Haber cycle for the solids, described by eqn (4). The trends for the alkalis and the lanthanides are summarized in Figs 3 and 4, respectively.

Due to the decreasing bulk cohesive energy and ionization potential of alkali elements with increasing atomic number, illustrated in Fig. 3, the reaction enthalpies of the heavier elements have larger negative values. This is indicative of a strongly exothermic intercalation process of such elements, in agreement with the experimental trends [4, 17]. Our results, shown in Fig. 3(c), indicate the  $M_3 C_{60}$  phase to be most stable, in agreement with experimental evidence. This is a consequence of the Madelung constant  $\alpha$  which is larger in the  $M_3 C_{60}$  structure than the  $MC_{60}$  structure. The further increase of the Madelung energy from the  $M_3 C_{60}$  to the  $M_6 C_{60}$  system is not sufficient to compensate an even stronger increase in the energy cost of the cohesion and ionization steps. A near-constant energy difference between the different phases for the whole alkali series supports our finding that the Madelung energy on the right-hand side of the Born–Haber cycle does not change much

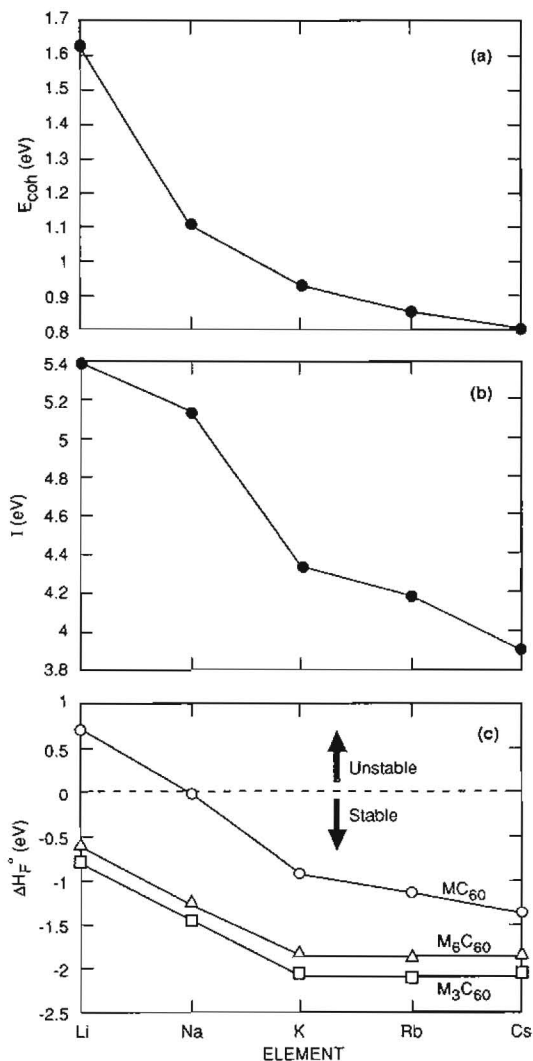


Fig. 3. Origin of stability trends for alkali-based  $M_xC_{60}$  solids. (a) Cohesive energies  $E_{\text{coh}}$  of alkali metals. (b) Ionization potentials  $I$  of alkali elements. (c) Formation enthalpies  $\Delta H_f^0$  of  $M_xC_{60}$  solids for  $x = 1, 3, 6$ .

between different alkali-based systems with the same stoichiometry.

The trends in the stability of the lanthanide series are investigated along the same lines in Fig. 4. For these systems, we also studied an alternative stoichiometry,  $M_2C_{60}$ , with either both tetrahedral (2T) interstitial sites in the  $C_{60}$  lattice occupied, or an occupation of one octahedral and one tetrahedral (O + T) interstitial site per unit cell. As shown in Fig. 4(c), the formation enthalpy  $\Delta H_f^0$  generally increases with an increasing number of  $4f$  electrons, loosely following the trend given by the total ionization potential  $I_{\text{tot}}(M)$ , given in Fig. 4(b). Again, the energy changes in the ionization step dominate over the changing energy of the atomization step shown in Fig. 4(a) [compare the energy scales of Fig. 4(a)

and (b)]. As in the case of alkali intercalants, the  $M_3C_{60}$  phase is most stable, and the energy difference between the different phases is nearly independent of the intercalant element. These results suggest that only early lanthanides should form stable intercalation compounds. These compounds are ideal candidates for novel  $C_{60}$  based superconductors.

Most of what has been said about the formation energetics of  $M_xC_{60}$  solids applies also to free  $M@C_{60}$  endohedral complexes. Also in the latter systems, changes in energetics of the Born-Haber cycle occur mainly in the atomic ionization step which is identical to the bulk compounds. Therefore, the predicted

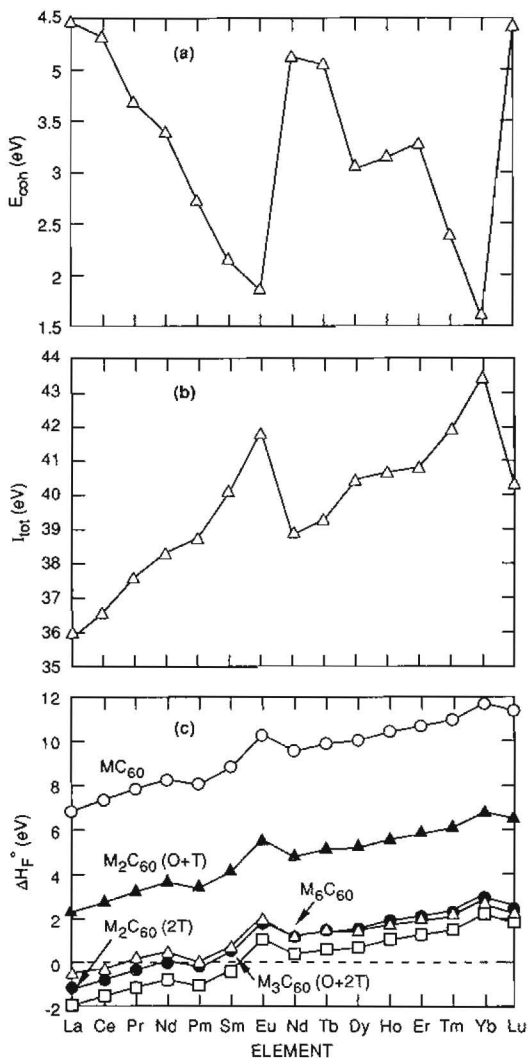


Fig. 4. Origin of stability trends for lanthanide based  $M_xC_{60}$  solids. (a) Cohesive energies  $E_{\text{coh}}$  of lanthanide metals. (b) Ionization potentials  $I$  of lanthanide elements. (c) Formation enthalpies  $\Delta H_f^0$  of  $M_xC_{60}$  solids for  $x = 1$  (fcc, only octahedral interstitial sites occupied),  $x = 2$  (fcc, both tetrahedral interstitial sites occupied, 2T),  $x = 2$  (fcc, one octahedral and one tetrahedral interstitial site occupied, O + T),  $x = 3$  (fcc, one octahedral and both tetrahedral interstitial sites occupied, O + 2T),  $x = 6$  (bcc phase).

stability of  $M@C_{60}$  systems mimics the trends set by the  $M_xC_{60}$  solids, as seen when comparing Fig. 2(a) and (b).

It is also instructive to have a closer look at the energetics of the relaxation step in the Born–Haber cycle for free  $M@C_{60}$  complexes. The relaxation energy  $E_{\text{relax}}$  and the equilibrium off-center distance of the  $M^{n+}$  ion inside the  $C_{60}^{n-}$  cage are determined by a competition between the polarization energy  $E_{\text{pol}}$  of the cage due to the moving ion, and the repulsion  $E_{\text{rep}}$  between the  $M^{n+}$  ion and the  $C_{60}^{n-}$  cage. As we discussed in [14],  $E_{\text{pol}}$  increases with the square of the charge transferred between  $M$  and  $C_{60}$ , whereas  $E_{\text{rep}}$  increases with increasing radius of the enclosed ion. While  $E_{\text{pol}}$  is nearly independent of the element within the same group in the periodic table,  $E_{\text{rep}}$  increases with increasing atomic number. Hence the off-center distance and the relaxation energy are both smaller for the heavier elements within the same group. On the other hand, the main difference between neighboring elements in the same row of the periodic table lies in their valency and not in the atomic radius. Since differences in the polarization energy dominate in this case, we expect an increase in the relaxation energy and off-center distance for elements which transfer a larger charge to the  $C_{60}$  cage.

An interesting quantity which can also be addressed by our formalism is the equilibrium oxidation state of  $M$ , and the effect of valency on the formation energy of  $M_xC_{60}$  and  $M@C_{60}$ . The oxidation state enters the Born–Haber cycle in the ionization step and in the following steps depending on the Coulomb energy of the system. Our results for the formation enthalpies of intercalation compounds based on late trivalent lanthanides such as  $\text{Eu}$  and  $\text{Yb}$  change dramatically if we consider these elements as divalent. In particular, we find the  $M_3C_{60}$  solids to be stable for  $M = \text{Eu}, \text{Yb}$  in their divalent form, while the trivalent counterparts are shown as unstable in Fig. 4 [13]. A similar stability change with changing valency can occur in free  $M@C_{60}$  endohedral complexes.  $\text{Sc}@C_{60}$ , shown as unstable for  $\text{Sc}^{3+}$ , becomes stable for  $\text{Sc}^{2+}$ , in analogy to the observed complex  $\text{Sc}@C_{82}$  which contains divalent scandium [18]. The presence of an encapsulated atom in  $C_{60}$  and its changing valency should have a pronounced effect on the optical spectra of  $C_{60}$  [19].

In this context, it is useful to outline the limits of our approach. The assumption of purely ionic bonding between the intercalants, which has firm support in donor systems, does not apply to that extent in acceptor systems. In systems such as  $\text{O}@C_{60}$ , a covalent interaction (in this case a strong “inside”

epoxy bond) between the intercalant and the  $C_{60}$  can tilt the energy balance towards stabilization [15].

#### 4. SUMMARY AND CONCLUSIONS

In summary, we developed a Born–Haber cycle to determine the stability of bulk  $M_xC_{60}$  intercalation compounds and free  $M@C_{60}$  endohedral complexes. The “thermodynamic” treatment of formation enthalpies and energies has been shown not only to yield numerical values which agree with available experimental data, but also to explain stability trends across the periodic table. In general we find donor elements of the groups IA, IIA and IIIB, as well early lanthanides and actinides, to form stable charge transfer compounds or complexes. Acceptor elements of the groups VIA and VIIA do not form stable charge transfer compounds or complexes. For the solids, we found  $M_3C_{60}$  to be generally the most stable stoichiometry. We anticipate a potential for superconductivity for some stable 3+ lanthanides and actinides in this phase, with a half-filled LUMO + 1 derived band of  $C_{60}$ , and for stable  $M_2C_{60}$  compounds of 2+ rare earth elements. Encapsulation of atoms is expected to modify the optical properties of the  $C_{60}$  cage. A hypothetical material composed of  $M@C_{60}$  molecules is expected to show superconducting behaviour and be governed by the same physics as that of solid  $M_xC_{60}$  intercalation compounds [20].

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