Lanthanide- and actinide-based fullerite compounds: potential A_xC_{60} superconductors?

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The stabilities of lanthanide and actinide intercalated fullerites are calculated with a Born–Hess thermodynamic cycle. For example, the calculated formation enthalpies indicate that the most likely superconducting phase of the Yb compound, $Yb_2^{3+}C_{60}^{4-}$, is metastable and may decompose into the insulating $Yb_3^{3+}C_{60}^{6-}$ and pristine C_{60} phases. Apart from the formation enthalpies, our calculations predict the equilibrium structure and stoichiometry, as well as intercalant valency, which are presently unknown in the Yb and other lanthanide and actinide intercalation compounds. We find some of these compounds, such as $La_3^{3+}C_{60}^{9-}$, to be excellent candidates for a new class of C_{60} based superconductors.

Inorganic compounds and organometallic molecules of lanthanide earths are known to be very ionic, with the lanthanides typically present in a 3+ state [1]. Organolanthanide chemistry has discussed thoroughly the electropositive character of these elements, and crystal structure studies have shown little participation of the 4f valence orbitals in the ionic bonds [2]. A similar situation occurs in organoactinides, where the bonds between the actinide earth elements and the organic moieties are strongly ionic, in spite of a participation of 5f valence orbitals in the bonds [2]. With this chemistry as a background, we have considered a model for intercalated fullerite solids having stoichiometries A_xC_{60}, with $x = 1, 2, 3, 6$, in which the lanthanide and actinide elements A are present as cations and the C_{60} molecules as anions.

We calculate the formation enthalpy of these fullerite intercalation compounds using a Born–Haber cycle, which has been successfully used to determine the stability of alkali and alkaline earth compounds [3]. Our calculations determine not only the stability, but also the equilibrium stochiometry, and possible reactions leading to the synthesis of the specific compounds. Our results indicate that the A_3C_{60} structure, which is isomorphic to K_3C_{60}, is the most stable phase for all rare earth compounds. In the case of trivalent intercalants, by analogy with the half-filled first LUMO of K_3C_{60} [4], we expect these A_3C_{60} solids to be metallic and possibly superconducting, since in this case the second lowest unoccupied molecular orbital (LUMO) of C_{60} with t_{1g} symmetry would be half-filled.

Fullerite, an fcc crystal [5] based on the C_{60} molecule [6], has been doped with various elements to yield room temperature conductors and low temperature superconductors [4,7–9]. The highest T_c reported to date is 33 K for Cs_2RbC_{60} [9]. We recently employed a Born–Haber cycle to calculate the stabilities of ionic solids AC_{60}, A_3C_{60}, and A_6C_{60}, with A alkali, or alkaline earth, elements [3]. The Born–Haber cycle yielded calculated stabilities, lattice constants, bulk moduli, and phonon spectra. The formation enthalpy per K for K_3C_{60} was lower than for K_6C_{60} [3], in qualitative agreement with the successful experimental use of the "back titration" method, in which first the bcc K_6C_{60} is made, and then extra C_{60} added to yield K_3C_{60} [10].

The fullerite intercalation compounds exist because of the stability of A_xC_{60} versus the stability of the components in their standard states, i.e. C_{60}(s) and A(s). It is a noteworthy fact that many of the elements incorporated by the Smalley group and others in C_{2n} fullerenes [11,12] [#1], yielding metallofullerene molecules $A@C_{2n}$, also occur in doped fullerite [4,7–9], among them the alkali elements and alkaline earth Ca. Weaver and co-workers have obtained evidence of compound formation between C_{60} and Y, Ca, Ba, Sr [14–16]. A notable exception to this correlation involves rare earth elements of the lanthanide, Ln, and actinide, An, series. Almost all lanthanides have been seen as metallofullerenes $Ln@C_{2n}$, with $Ln@C_{82}$ soluble in solvents that extract fullerenes [17–21]. U appears to be an actinide voracious in its capacity for $U@C_{2n}$ formation [22]. Because all of the elements that have been seen as metallofullerenes are electropositive elements, and a sub-class of these elements have resulted in intercalated fullerites, we decided to apply the Born–Haber cycle method [3] to the lanthanide and actinide compounds. In this regard, we are encouraged to see that organolanthanide and organoactinide molecules show strong evidence for ionic bonds [1,2], which suggests that a treatment of an assumed ionic solid A_xC_{60}, $A = Ln$ or An, is reasonable.

The formation enthalpy $\Delta H_f^0(A_xC_{60})$ of A_xC_{60} at $T = 0$ K is defined by

$$xA(\text{solid}) + C_{60}(\text{solid}) \xrightarrow{x\Delta H_f^0} A_xC_{60}(\text{solid}) \quad (1)$$

and can be estimated using the Born–Haber cycle which is shown in fig. 1. We find

$$x\Delta H_f^0 = xE_{\text{coh}}(A) + E_{\text{coh}}(C_{60}) + xI_{\text{tot},n}(A)$$
$$- A_{\text{tot},nx}(C_{60}) - E_{\text{coh}}(A_x^{n+}C_{60}^{nx-}) . \quad (2)$$

The compound A_xC_{60}(solid) is stable when ΔH_f^0 is negative. The individual steps and the procedure to estimate the corresponding reaction enthalpies are explained in detail in ref. [3]. We approximated each step by the corresponding energy and hence have neglected the contributions of nonzero temperature and pressure to ΔH_f^0, which we estimate to be of the order of $\lesssim 0.1$ eV. Briefly, the assumed structures are fcc for the A_xC_{60}, $x = 1, 2, 3$, and bcc for A_6C_{60}. In
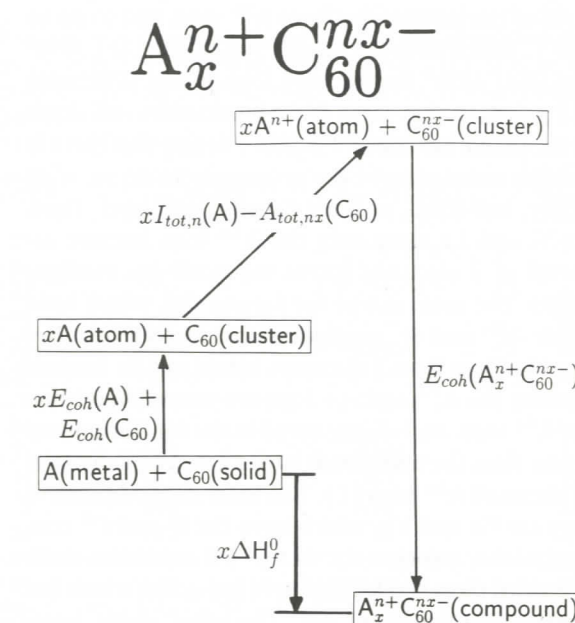
[#1] For $Ca@C_{60}$, see ref. [13].

Fig. 1. Born–Haber cycle used to predict the formation enthalpy ΔH_f^0 of donor C_{60} fullerite intercalation compounds.

eq. (2) $E_{\text{coh}}(A)$ is the bulk binding energy of A [#2], and $E_{\text{coh}}(C_{60}$ solid) is the corresponding binding energy of a C_{60} molecule in C_{60} (solid). $I_{\text{tot},n}$ and $A_{\text{tot},n}$ are the total ionization potentials and electron affinities, respectively, which stand for the total energy difference between the final state with the total charge $(n+)$ or $(n-)$ and the neutral initial state [3]. For the ionic compound, we find

$$-E_{\text{coh}}(A_x^{n+}C_{60}^{nx-})$$
$$= E_{\text{Madelung}} + E_{\text{BM}} - \tfrac{1}{2}ZD(C_{60}^{nx-} - C_{60}^{nx-}) , \quad (3)$$

where E_{Madelung} is the Madelung energy per unit cell, and E_{BM} is the Born–Mayer repulsive energy, as discussed in detail in ref. [3]. We assume here a complete transfer of n electrons from the intercalant to C_{60}, and have treated cases where $n = 2$ and 3. D is the dissociation energy of a pair of C_{60} molecules, and Z denotes the coordination number of the C_{60} molecules, equal to 12 in the close-packed fcc structure and 8 in the bcc structure.

[#2] The observed cohesive energies for most elements are given in ref. [23]. The estimated value $E_{\text{coh}} = 2.75$ eV for Pm has been obtained by interpolating the values of the neighboring lanthanide elements.

All of the lanthanides form A^{3+} ions, and so do Sc and Y, which have the atomic structures [Ar] $3d4s^2$ and [Kr] $4d5s^2$, respectively. Cotton and Wilkinson [1] point out that some of the lanthanides will occur in the oxidation states +2 and +4, and that there is a rough correlation of the propensity to do so, if an empty, half-filled, or filled f shell is obtained. Thus, Sc, Y, and La form only the A^{3+} ions because removal of 3 electrons leaves the noble-gas configuration. The same is true for Lu and Gd, which have stable $4f^{14}$ and $4f^7$ configurations, respectively. Removal of less than 3 electrons would not be favored because the A^{2+} and A^+ ions are much larger than the A^{3+} ions, and energy saved in the ionization step is less than the additional lattice energy of the salts of the small A^{3+} ions [1]. The most stable dipositive ions are Eu and Yb, which have the f^7 and f^{14} configurations, respectively, in the +2 oxidation state. The third most stable dipositive ion is Sm, which has electron configuration $4f^6$. The most stable tetrapositive ions are Ce and Tb, which have the f^0 and f^7 configurations, respectively, in the +4 oxidation state. This "special stability" rule is not absolute in the lanthanide series. For example, Ce and Pr have been identified in the +2 oxidation state, and Pr and Nd the +4 oxidation state, although these are generally much less stable compounds [1]. Accordingly, we have treated Sm, Eu, and Yb as if they could exist as +2 or +3 ions.

We extended our calculations of the Madelung energy, as described in ref. [3], to A_2C_{60}(2T) (A occupying both tetrahedral interstitial sites in the unit cell) and A_2C_{60}(O+T) (one octahedral and one tetrahedral A interstitial site filled). In the latter case, we assumed that the cubic symmetry of the lattice is preserved. The Madelung constants are $\alpha_{2T}=11.637$ and $\alpha_{O+T}=10.773$. The total electron affinity A_{tot} of C_{60} has been estimated along the lines of ref. [3]. For the stoichiometries not discussed there, we found $A_{tot}(C_{60}^{4-})=-4.16$ eV, $A_{tot}(C_{60}^{9-})=-83.15$ eV, and $A_{tot}(C_{60}^{18-})=-452.06$ eV [#3]. These values are based on the assumption that the energy difference between the LUMO and LUMO+1 is 0.61 eV [24].

[#3] Electron affinities are calculated from energy differences of neutral and charged molecules. Negative electron affinities cannot be observed for isolated gas-phase molecules, but do have a relevance in the Born–Haber cycle for the solid.

Table 1 shows the calculated formation enthalpies of the lanthanide and actinide compounds $A^{+3}C_{60}^{3-}$ (O), $A_2^{+3}C_{60}^{6-}$ (2T), $A_3^{+3}C_{60}^{9-}$ (O+2T), and $A_2^{+3}C_{60}^{6-}$ (O+T), and $A_6^{+3}C_{60}^{18-}$ (bcc) in the 3+ oxidation state. Table 2 shows the corresponding formation enthalpies of the Sm, Eu, and Yb compounds for the 2+ oxidation state. Note that the formation enthalpy is given per intercalant atom in all the figures.

From our results presented in tables 1 and 2, the compounds A_3C_{60} with all tetrahedral and octahedral sites in the fcc structure filled are the most stable and can be formed for the initial components in their standard state, as indicated by the negative sign of ΔH_f^0. For a less than half-filled or more than half-filled f shell, we find that the stability of A^{3+} lanthanide compounds decreases with increasing number of f electrons, closely following a corresponding increase of the ionization potential. In most of the cases discussed here, the energy gain per intercalant atom in the A_6C_{60} phase is substantially smaller than in the A_3C_{60} phase. In order to investigate which is the saturated phase, we consider the reaction

$$A_3C_{60}+3A(\text{metal}) \xrightarrow{\Delta H} A_6C_{60}. \qquad (4)$$
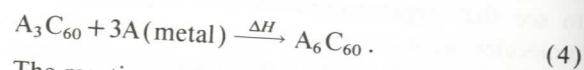
The reaction enthalpy is related to the heats of formation of the different compounds by $\Delta H=6\Delta H_f^0(A_6C_{60})-3\Delta H_f^0(A_3C_{60})$. We find ΔH to be positive for almost all compounds considered here, corresponding to an endothermic process and indicating that A_3C_{60} is the saturated phase. The only case where ΔH is negative (and A_6C_{60} is the saturated phase) are the actinide compounds of Ac^{3+} (-5.58 eV) and U^{3+} (-8.67 eV). Very small positive values of ΔH are found for Sm^{2+}, Eu^{2+} and Yb^{2+}, indicative of an at least metastable A_6C_{60} phase. In the cases where A_6C_{60} is stable, the A_3C_{60} compound can be synthesized in an exothermic "back titration" reaction, by mixing the pristine C_{60} solid and the saturated compound, as

$$C_{60}(\text{solid})+A_6C_{60} \xrightarrow{\Delta H} 2A_3C_{60}. \qquad (5)$$
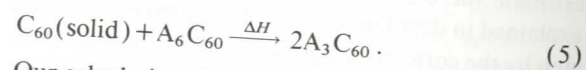
Our calculations indicate that the A_2C_{60} phase is the second most stable phase in most cases. We find the phase with both tetrahedral sites filled to be more stable than the phase with one tetrahedral and one octahedral site per unit cell. The main reason for this

Table 1
Predicted formation enthalpies ΔH_f^0 (eV) for different C_{60} fullerite intercalation compounds A_xC_{60}, for the (3+) state of the intercalant. Five different phases are considered: A_1C_{60} (fcc structure), A_2C_{60} (fcc structure, both tetrahedral sites filled), A_2C_{60} (fcc structure, one tetrahedral and one octahedral site filled), A_3C_{60} (fcc structure, all tetrahedral and octahedral sites filled), A_6C_{60} (bcc structure). Results are presented for elements A from the lanthanide and actinide rare earth series

	A	AC_{60} (fcc, O)	A_2C_{60} (fcc, 2T)	A_2C_{60} (fcc, O+T)	A_3C_{60} (fcc, O+2T)	A_6C_{60} (bcc)
lanthanide compounds	La^{3+}	6.83	−1.27	2.28	−1.96	−0.49
	Ce^{3+}	7.37	−0.86	2.74	−1.58	−0.31
	Pr^{3+}	7.82	−0.41	3.20	−1.13	0.15
	Nd^{3+}	8.25	−0.05	3.59	−0.78	0.40
	Pm^{3+}	8.03	−0.33	3.33	−1.07	0.01
	Sm^{3+}	8.76	0.37	4.05	−0.37	0.67
	Eu^{3+}	10.20	1.76	5.46	1.01	1.95
	Gd^{3+}	9.52	1.04	4.76	0.29	1.19
	Tb^{3+}	9.83	1.31	5.05	0.54	1.35
	Dy^{3+}	9.95	1.39	5.14	0.63	1.39
	Ho^{3+}	10.30	1.73	5.49	0.96	1.68
	Er^{3+}	10.56	1.94	5.72	1.16	1.80
	Tm^{3+}	10.84	2.19	5.98	1.40	2.01
	Yb^{3+}	11.56	2.89	6.70	2.10	2.67
	Lu^{3+}	11.21	2.52	6.34	1.73	2.26
actinide compounds	Ac^{3+}	4.94	−3.38	0.27	−4.12	−2.99
	Th^{3+}	10.28	1.63	5.43	0.85	1.45
	U^{3+}	6.78	−2.18	1.76	−3.01	−2.95

Table 2
Predicted formation enthalpies ΔH_f^0 (eV) for selected C_{60} fullerite intercalation compounds A_xC_{60}, for the (2+) state of the lanthanide intercalants. Five different phases are considered: A_1C_{60} (fcc structure), A_2C_{60} (fcc structure, both tetrahedral sites filled), A_2C_{60} (fcc structure, one tetrahedral and one octahedral site filled), A_3C_{60} (fcc structure, all tetrahedral and octahedral sites filled), A_6C_{60} (bcc structure)

	A	AC_{60} (fcc, O)	A_2C_{60} (fcc, 2T)	A_2C_{60} (fcc, O+T)	A_3C_{60} (fcc, O+2T)	A_6C_{60} (bcc)
lanthanide compounds	Sm^{2+}	1.20	−2.17	−0.80	−2.91	−1.32
	Eu^{2+}	1.12	−2.30	−0.91	−3.04	−1.49
	Yb^{2+}	2.36	−1.40	0.13	−2.15	−0.91

fact is the repulsion between the cations in adjacent tetrahedral and octahedral sites which reduces the Madelung constant. Obviously, the smaller interionic repulsion in the larger octahedral site is only of secondary importance. As in our calculation of the alkali and alkaline earth compounds [3], we find AC_{60} with NaCl structure to be the least stable phase.

A by-product of our calculations are lattice constants and bulk moduli which in general follow the trends discussed in ref. [3]. The large Madelung energies exert a pressure on the lattice and reduce the lattice constants by typically 10% with respect to pristine C_{60} in the fcc phase and by up to 30% in the more ionic bcc phase. Since the bonding character changes from mostly van der Waals in pristine C_{60} to ionic in the intercalation compounds, the bulk modulus increases typically by an order of magnitude upon intercalation. The details will be discussed elsewhere [25].

The high symmetry of the C_{60} molecules leads to highly degenerate orbitals. The LUMO with a t_{1u} character and the LUMO+1 with a t_{1g} character [26]

spread into narrow bands in the solid [27]. In $A_3^+ C_{60}^-$ compounds such as $K_3^+ C_{60}^{3-}$, the t_{1u} derived band is half filled which leads to conductivity and superconductivity of the crystal. Consequently, complete filling of this t_{1u} derived band, such as in $K_6^+ C_{60}^{6-}$, leads to a sharp drop of the conductivity. If the "rigid band" model of intercalation still holds for the rare earth compounds, and the intercalants do not hybridize with the matrix, we could expect conductivity and superconductivity upon partial filling of the t_{1u} derived band, such as in $A_2^{2+} C_{60}^{4-}$. As mentioned above, and also shown in table 2, the heat of formation of $Yb_2^{2+} C_{60}^{4-}$ from the initial components is large, even though smaller in magnitude than that of $Yb_3^{3+} C_{60}^{6-}$. Should a metastable $Yb_2^{2+} C_{60}^{4-}$ phase coexist with the stable $Yb_3^{3+} C_{60}^{6-}$ phase, such a compound could possibly show superconductivity, which has been observed recently [28]. Nevertheless, our calculations indicate that such a compound should spontaneously phase separate into $Yb_3^{3+} C_{60}^{6-}$ and C_{60} on energetic grounds.

Another class of potential rare earth based superconductors are the $A_3^{3+} C_{60}^{9-}$ compounds. In this case, conductivity and superconductivity should result from partial filling of the t_{1g} derived band of C_{60} fullerite. Since $A_3 C_{60}$ is the most stable phase, compounds of all early lanthanides and some of the actinides might be good candidates for such superconductors. As the density of states at the Fermi level, and accordingly the value of T_c, increases with increasing lattice constant [29], we anticipate $La_3^{3+} C_{60}^-$ to give one of the highest T_c values.

In conclusion, we found that most lanthanide and actinide rare earth elements form stable C_{60} fullerite intercalation compounds. The stable stoichiometry, corresponding to the saturated phase in most cases, is $A_3 C_{60}$. We anticipate a potential for superconductivity for some 3+ lanthanides and actinides in this phase, with a half-filled LUMO+1 derived band of C_{60}. A second possibility for superconducting compounds is suggested for the $A_2 C_{60}$ of 2+ rare earth elements. This phase, however, is found to be thermodynamically metastable or unstable with respect to the $A_3 C_{60}$ and pristine C_{60} phases which are insulating. In particular, the elements Sm, Eu, and Yb should be the easiest for the experimentalist to work with, because their cohesive energies are dramatically lower than those of the other lathanide solids [#4].

To succeed in mixing C_{60} with the other lanthanide elements, which could lead to formation of the intercalation compounds discussed here, will likely be more challenging.

[#4] For example, the cohesive energy of Eu is 1.86 eV, while that of La is 4.47 eV (see footnote 2).

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