Structural Stability of Vacancy-ordered Yb$_{2.75}$C$_{60}$

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The fcc-based structure of Yb$_{2.75}$C$_{60}$ is unique among metal-doped fullerene compounds, exhibiting long-range-ordered vacancies, significantly off-centered divalent Yb cations, and distorted, crystallographically inequivalent, orientationally ordered C$_{60}$ anions. A simple electrostatic-energy analysis, which models the constituents using point charges, is shown to provide insight into how each of these features stabilizes this unusual crystal structure. The results have general implications for a variety of other intercalated metal fullerides.

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Since 1991, numerous superconducting compounds of C$_{60}$ intercalated with monovalent alkali and divalent alkaline-earth metals have been prepared and structurally characterized$^1$. In many respects, their crystal structures can be described by regarding the C$_{60}$ anions as large, negatively-charged “atoms” forming simple fcc or bcc lattices, the interstices of which are filled by metal cations. The stability of these structures is generally well understood within simple models dominated by electrostatic energies$^2$$^3$. The analysis of the structural energetics through more complete first-principles calculations confirms and refines the simple models$^1$.

Ytterbium metal has also been shown to form a superconducting compound with C$_{60}$, but with a structure that is considerably more complex$^4$. It can be viewed as a modification of a hypothetical Yb$_3$C$_{60}$ structure, analogous to that of K$_3$C$_{60}$$^5$ and schematically illustrated in Fig. 1(a). In this ideal Yb$_3$C$_{60}$ structure, Yb cations sit at the centers of the octahedral (O) and tetrahedral (T) holes created by the fcc lattice of pure C$_{60}$. Systematically removing 1 of the 8 T-cations leads to the ordered-vacancy structure of Yb$_{2.75}$C$_{60}$ in Fig. 1(b), where the full unit cell is seen to contain 8 subcells, each with a different T-site vacancy. One such subcell, with the C$_{60}$

FIG. 1. (a) Schematic picture of hypothetical fcc Yb$_3$C$_{60}$ structure (C$_{60}$ anion radius is 3.5 Å, Yb$^{2+}$ radius is 1.0 Å). Cations fill all tetrahedral (T) and octahedral (O) interstitial sites and are shaded gray and black, respectively. Removing one T-site cation (shown with arrow) leads to the fcc-based vacancy-ordered Yb$_{2.75}$C$_{60}$ structure in (b), with the C$_{60}$ anions removed for clarity. Eight subcells comprise the full unit cell. In the expanded subcell shown, O-site cations are significantly displaced from their ideal, “centered” positions towards the nearest vacancy, and each T-site cation is displaced less (drawn exaggerated) along one of the Cartesian axes. Other O-site cations have been displaced towards vacancies in adjacent subcells. (c) Same Yb$_{2.75}$C$_{60}$ subcell as in (b) but with the Yb cations omitted. The vacancies create 3 inequivalent types of C$_{60}$ anions, schematically shown with different shadings and shapes. Each anion rotates about the local axis indicated, to maximize the number of pentagon faces oriented towards the surrounding cations.
anions removed for clarity, highlights the large displacements of the O-cations towards their nearest-neighbor (NN) vacancy and the smaller displacements of the T-cations along Cartesian axes $\mathbf{b}$. The 3 types of crystallographically inequivalent $\text{C}_{60}$ anions with 2, 1, or 0 neighboring vacancies, and their correspondingly different coordinates of 12, 10, and 8 Yb cations, are shown in Fig. 1(c). Also included schematically are the different distortions of the anions $\mathbf{r}$ and the local axes about which they rotate in order to orient their pentagonal faces towards the NN cations.

In this Letter, we identify the underlying reasons for the stability of this apparently exotic phase. A simple electrostatic model is used to evaluate the energies associated with vacancy formation, cation displacements, and $\text{C}_{60}$ orientations and distortions. Our analysis shows that the latter relaxation energies more than compensate the cost of creating a Yb vacancy. The formation of $\text{Yb}_{2.75}\text{C}_{60}$ is therefore seen to fit naturally into a unified understanding of both the stability of metal-doped $\text{C}_{60}$ compounds and the role of particular structural defects.

Our investigation focuses on understanding why the ideal $\text{Yb}_3\text{C}_{60}$ structure in Fig. 1(a) is not formed but is instead found to phase separate into the observed $\text{Yb}_{2.75}\text{C}_{60}$ structure and Yb metal. For these two structures, we compare the relative energies of steps in a Born-Haber cycle, taken with respect to a reference system of undoped fcc $\text{C}_{60}$ and isolated neutral Yb atoms. The steps are (i) ionizing the Yb atoms into Yb$^{2+} + 2e^-$, (ii) condensing any excess Yb atoms into Yb metal, (iii) completely transferring the ionized electrons from Yb to the $\text{C}_{60}$ molecules, and (iv) assembling the cations and anions into a crystal. Since the electrostatic energy is the largest single contribution to the structural energetics in these systems, it is expected to dominate the energy differences between the configurations of interest. Accordingly, we approximate the relative energies in steps (iii) and (iv) by the electrostatic energy differences alone. The ions are modeled using point charges, and the Ewald method $\mathbf{E}$ is used to evaluate the resulting Coulombic sums. Experimental structural parameters are used to incorporate the effects of short-range repulsive interactions between the Yb cations and $\text{C}_{60}$ anions. The parameters from Ref. 5 are slightly simplified by taking $a = b = c = 27.8733$ Å (i.e., ignoring the $< 0.4\%$ orthorhombic distortion) and by assuming complete occupation of the octahedral sites. All energies are given in eV per $\text{Yb}_3\text{C}_{60}$ formula unit, or equivalently, in eV/$\text{C}_{60}$.

We begin by computing the relative formation energies of two hypothetical structures, ideal $\text{Yb}_3\text{C}_{60}$ and “unrelaxed” $\text{Yb}_{2.75}\text{C}_{60}$. The latter is obtained by removing the requisite Yb T-cations from an ideal $\text{Yb}_3\text{C}_{60}$ lattice to form the ordered-vacancy structure in Fig. 1(b), while keeping all the remaining cations at the centers of their respective O- and T-site holes. The ionization steps for ideal $\text{Yb}_3\text{C}_{60}$ and unrelaxed $\text{Yb}_{2.75}\text{C}_{60}$ involve, respectively, 3 Yb atoms with an energy $E_{\text{ion}} = 55.29$ eV and 2.75 Yb atoms with $E_{\text{ion}} = 50.68$ eV $\mathbf{[1]}$. The excess 0.25 Yb atom per $\text{C}_{60}$ in $\text{Yb}_{2.75}\text{C}_{60}$ is condensed into Yb metal, giving a cohesive energy gain $E_{\text{coh}} = -0.4$ eV $\mathbf{[1]}$. The total electron affinity for transferring 6 electrons to $\text{C}_{60}$ in $\text{Yb}_3\text{C}_{60}$ is approximated as 6 times the first electron affinity for $\text{C}_{60}$ $\mathbf{[2]}$ plus the electronic self-energy, which is modeled as the minimum energy of 6 classical point electrons on a uniform spherical shell of radius 3.5 Å $\mathbf{[3]}$; the result is a net energy cost $E_{\text{ca}} = -15.90 + 41.04 = 25.14$ eV. The analogous energy for transferring 5.5 electrons to $\text{C}_{60}$ in $\text{Yb}_{2.75}\text{C}_{60}$ is approximated by interpolating the self-energy between integer numbers of electrons $n = 2, 3, 4,$ and 6 with a second-order polynomial in $n$, yielding $E_{\text{ca}} = -14.58 + 33.17 = 18.59$ eV. Finally, the Yb cations and $\text{C}_{60}$ anions are assembled into their respective fcc-based crystal structures, differing only by the T-site vacancies in unrelaxed $\text{Yb}_{2.75}\text{C}_{60}$. The Madelung energies, computed by treating the Yb cations as points with charge $2+$ and replacing the spherical shells of the $\text{C}_{60}$ anions with points of charge 6− or 5.5−, are $E_{\text{Mad}} = -91.43$ eV for $\text{Yb}_3\text{C}_{60}$ and $-77.65$ eV for $\text{Yb}_{2.75}\text{C}_{60}$. Comparing the total formation energy $E_{\text{form}} = E_{\text{ion}} + E_{\text{coh}} + E_{\text{ca}} + E_{\text{Mad}} = -11.00$ eV for ideal $\text{Yb}_3\text{C}_{60}$ with $E_{\text{form}} = -8.78$ eV for unrelaxed $\text{Yb}_{2.75}\text{C}_{60}$ shows that the larger Madelung energy gain in forming $\text{Yb}_3\text{C}_{60}$ exceeds its larger ionization and self-energy costs, and thus creating T-site vacancies in unrelaxed $\text{Yb}_{2.75}\text{C}_{60}$ is endothermic: $\Delta E_{\text{form}} = 2.22$ eV.

The possible relaxation-energy gains associated with vacancy formation must now be considered. One obvious source is the displacement of each O-site Yb cation towards its NN vacancy (see Fig. 1(b)). The equilibrium value for this displacement, determined by the balance of electrostatic forces and short-range repulsion between the cations and their neighboring anions, is known from experiment to be extremely large (2.41 Å $\mathbf{[4]}$): using this value leads to a computed energy gain of $-2.32$ eV. The much smaller off-center displacements of the T-site cations (∼0.3 Å) contribute just $-0.009$ eV on their own, but combined with those of the O-site cations lead to a small cooperative interaction and a total relaxation-energy gain $E_{\text{displ}} = -2.40$ eV.

The above calculations assumed that the charges on all $\text{C}_{60}$ anions are given by the average number of electrons per $\text{C}_{60}$, namely $-5.5e^{-}$. The crystallographic inequivalence of the anions (see Fig. 1(c)), however, makes favorable the prospect of transferring electrons from $\text{C}_{60}$ (1), with 12 NN cations, to $\text{C}_{60}$ (3), which has only 8 $\mathbf{[5]}$. We investigate this possibility by allowing the inequivalent $\text{C}_{60}$ (1), $\text{C}_{60}$ (2), and $\text{C}_{60}$ (3) anions to have correspondingly different charges $-q_1e^-$, $-q_2e^-$, and $-q_3e^-$, with the only constraint being that $(q_1+6q_2+q_3)/8 = 5.5$. Minimizing the quantity $E_{\text{displ}} + E_{\text{ca}}$ with respect to $q_1$, we find $q_1 = 6.3$, $q_2 = 5.5$ and $q_3 = 4.7$. The charge of $\text{C}_{60}$ (2) is unchanged, while $0.8e^-$ is indeed transferred from
This is not a charge disproportionation but is rather a charge redistribution, reminiscent of the different charge states of the crystallographically inequivalent planar and chain O anions in YBa$_2$Cu$_3$O$_7$ [4]. We calculate that in Yb$_{2.75}$C$_60$ the associated energy gain $E_{\text{redist}}$ is just $-0.17$ eV. This small value reflects the nonlinear self-energy of electrons on C$_60$, and shows that the redistribution process plays only a minor role in determining structural stability. The magnitude of the relaxation energy gain in Yb$_{2.75}$C$_60$ of $E_{\text{disp}} + E_{\text{redist}} = -2.57$ eV is, within the estimated accuracy of our calculations, essentially equal to $\Delta E_{\text{form}} = 2.22$ eV.

We now consider the additional relaxation energy that can come from optimizing the orientation of the C$_60$ anions with respect to their anisotropic environment of NN cations. The largest contribution to the orientation energy is the electrostatic interaction between the charge density of electrons transferred to C$_60$, anisotropically distributed over its surface, and the neighboring Yb$^{2+}$ cations [3]. To calculate this orientational interaction energy obviously requires going beyond approximating the C$_60$ anions as uniformly charged spherical shells. Based on comparisons with chemical analogs [15,16] and first-principles calculations of C$^{-3}_{60}$ [17], which show that the transferred charge density is primarily associated with the pentagons, we model a C$_60$ anion as a truncated icosahedron with equal point charges localized at the centers of its 12 pentagonal faces and positioned 3.5 Å from its origin [17]. For a single cation neighbor, the C$_60$ anion will orient itself to minimize the distance between one of the point charges and the cation, mimicking the preference for a cation to be over a pentagonal face. Such an attraction between C$_60$ pentagonal faces and neighboring cations was first observed in (Ba$^{2+}$)$_3$C$_6$ and was found to be an important component in achieving the best Rietveld refinement of the Yb$_{2.75}$C$_60$ structure [18].

The orientational interaction energy, $E_{\Theta}$, was investigated using the set of {111} axes established in the x-ray structural determination [2]: these axes are shown in Fig. 2(c). Each C$_60$ anion is rotated by the same angle $\Theta$ around its own local axis. While these displacements are somewhat smaller than those inferred from the EXAFS data [3], suggesting that the absolute distortion energies are underestimated by our model, the scale of the difference $\Delta E_{\text{dis}}$ indicates that the distortion contribution to the total relaxation energy is relatively minor.

Our comparison of relevant energies in forming the Yb$_{2.75}$C$_60$ and Yb$_3$C$_60$ structures provides strong support for the central role played by the interaction between the anisotropically positioned Yb cations and the anisotropically distributed charge on the C$_60$ anions. As shown here, this strong interaction can be investigated through a relatively straightforward analysis of electrostatic energies, and does not require invoking any chemical behavior peculiar to Yb. Despite its simple form, the interaction has a profound effect on compound formation and crystal structure. In particular, application of
our model gives insight into the stability of a seemingly unwieldy structure involving both long-range-ordered vacancies in a 208-atom unit cell and crystallographically inequivalent C_{60} anions with low-symmetry cation coordinates. The relationship between these unusual structural features is now clear: A T-site cation vacancy leads to the O-site cation displacements, which in turn amplify the orientational cation-anion interactions. Only one vacancy per subcell is needed to induce displacements of all O-cations, making the formation of additional vacancies unfavorable. This naturally accounts for the observed Yb_{2.75}C_{60} stoichiometry.

One consequence of this simple picture is that the same ordered-vacancy phase for Yb_{2.75}C_{60} should be observed in fulleride compounds containing other divalent cations whose ionic radii and elemental cohesive energies are similar to Yb. Such expectations are, in fact, realized for both Ca- and Sm-doped C_{60}. Since the magnitudes of the electrostatic energies scale quadratically with charge, it might also be expected that many of the stabilizing factors identified here for these divalent-cation fullerides should occur for the similarly-sized monovalent Na cation. However, neither a Na\textsubscript{2}C_{60} structure nor a vacancy-ordered fulleride phase is observed; instead, a structural stability of this system.

The structural energetics of the systems in which T-site vacancies are observed, e.g., Rb\textsubscript{2}C_{60}, our analysis leads unavoidably to the conclusion that the surrounding O-site cations will undergo off-center displacements towards that vacancy (see Fig 1(b)). While this applies only to the fraction of O-site cations immediately surrounding the vacancies, such displacements should be detectable with appropriate measurements.

The model presented here is designed to capture the essential features of the structural energetics of the systems of interest, and to enhance the understanding of the origin and properties of complex structures. In Yb_{2.75}C_{60}, we found that the relaxation energies associated with the lowered symmetry are crucial in stabilizing its formation. The quantitative limitations of this type of analysis are clear. However, our model can provide valuable guidance for future, more definitive investigations of structural energetics in this and similar systems using first-principles calculations, and for designing and interpreting related experiments in the interim.

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