Vacancy-induced structural relaxations in $Yb_{2.75}C_{60}$

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The well-characterized vacancy-ordered structure of $Yb_{2.75}C_{60}$ can be understood within a simple electrostatic-energy model. The results provide valuable insight into how vacancies induce local structural relaxations, and are qualitatively transferable to cation vacancies in other intercalated metal fullerides. [S0163-1829(98)51426-9]

As the study of metal-intercalated C_{60} compounds has progressed,[1] increasing interest has been focused on how, or whether, the presence of cation vacancies can influence their properties. Specifically, cation vacancies might be expected to affect carrier concentration, as well as local electronic and crystal structure.[2–5] Proposals that these effects play an important role in superconductivity[6] and the low-temperature splitting of tetrahedral NMR lines[7,8] have proved controversial.[9,10] While theoretical investigations of vacancies could shed light on these issues, they unfortunately are extremely limited, with only one very recent study of the effect on the electronic density of states[11] and no available results on local structural relaxations.

The ordered-vacancy compound $Yb_{2.75}C_{60}$ (Ref. 12) offers a unique opportunity for theoretical investigation of the relationship between vacancies and structure. The idea is to identify the essential features of a model which can reproduce the local structural relaxations in $Yb_{2.75}C_{60}$, the experimental determination of which is facilitated by the *ordered* arrangement of the vacancies. The crystal structure of this fulleride, with 2008 atoms per unit cell, is already quite complex. It can be viewed as a modification of a hypothetical Yb_3C_{60} compound, analogous to K_3C_{60} (Ref. 13) and schematically illustrated in Fig. 1(a). In the ideal Yb_3C_{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}.

FIG. 1. (a) Schematic picture of hypothetical fcc Yb_3C_{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 three 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.
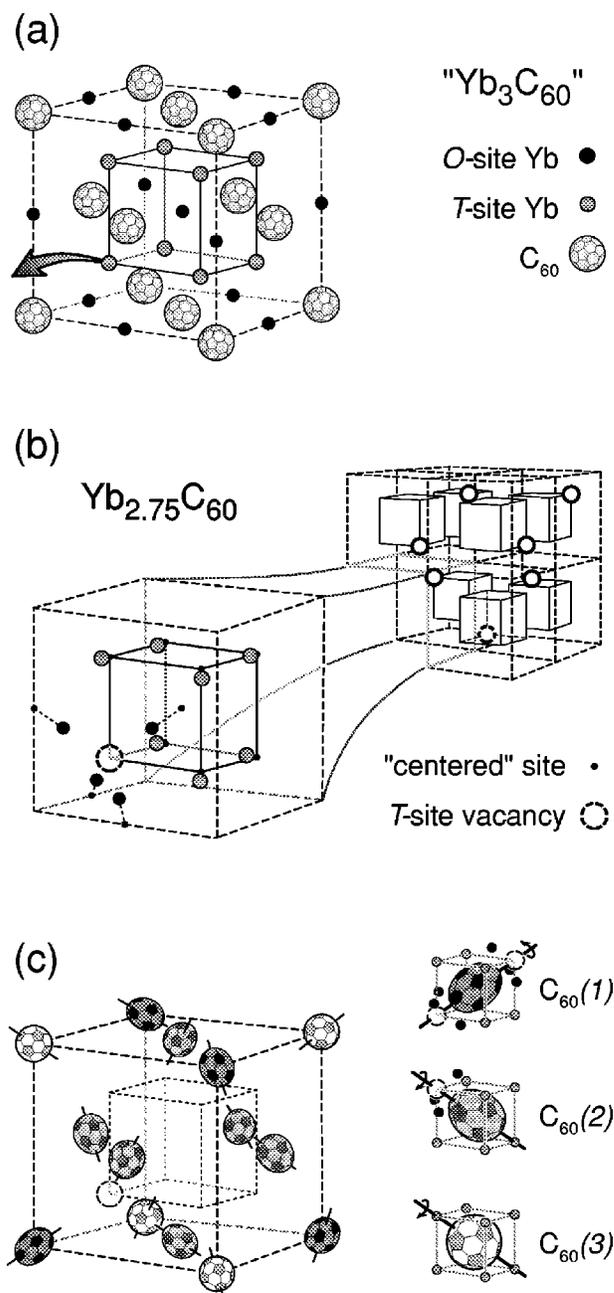
Systematically removing one of the eight T cations leads to the ordered-vacancy structure of $Yb_{2.75}C_{60}$ in Fig. 1(b), where the full unit cell is seen to contain eight subcells, each with a different T-site vacancy. One such subcell, with the C_{60} anions removed for clarity, highlights the large displacements of the O cations towards their nearest-neighbor (NN) vacancy and the smaller displacements of the T cations along Cartesian axes.[12] The three types of crystallographically inequivalent C_{60} anions with 2, 1, or 0 neighboring vacancies, and their correspondingly different coordinations of 12, 10, and 8 Yb cations, are shown in Fig. 1(c). Also included schematically are the different distortions of the anions[14] and the local axes about which they rotate in order to orient their pentagonal faces towards the NN cations.

In this paper, we show that the effects of T-cation vacancies on the structure of $Yb_{2.75}C_{60}$ can be understood within a simple electrostatic model. This allows us to evaluate the dominant contributions to the energies associated with all of the structural features described above: vacancy formation, cation displacements, and C_{60} orientations and distortions. While the results are inherently not highly quantitative, they do serve to rationalize these very different types of structural relaxations and to establish a hierarchy of energies associated with them. Furthermore, because the model used here does not incorporate any features specific to Yb-C_{60} bonding, these results can be applied more generally to the broader class of alkali-metal and alkaline-earth fullerides.

Our analysis of vacancy energetics focuses on the comparison of the fully occupied ideal Yb_3C_{60} structure in Fig. 1(a) with a phase-separated mixture of the observed vacancy-ordered $Yb_{2.75}C_{60}$ structure and Yb metal. For these two structures, we compute the relative energies of steps in a Born-Haber cycle, taken with respect to a reference system of undoped fcc C_{60} and isolated neutral Yb atoms. The steps are (i) ionizing the Yb atoms into $Yb^{2+} + 2e^{-}$,[15] (ii) condensing any excess Yb atoms into Yb metal, (iii) completely transferring the ionized electrons from Yb to the C_{60} molecules, and (iv) assembling the cations and anions into a crystal. Since the electrostatic energy is clearly 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 with point charges, and the Ewald method[16] is used to evaluate the resulting Coulomb sums. Experimental structural parameters are used to incorporate the effects of short-range repulsive interactions between the Yb cations and C_{60} anions. The parameters from Ref. 12 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 Yb_3C_{60} formula unit, or equivalently, in eV/C_{60}.

We begin by computing the relative formation energies of two hypothetical structures, ideal Yb_3C_{60} and "unrelaxed" $Yb_{2.75}C_{60}$. The latter is obtained by removing the requisite Yb T cations while keeping the remaining cations frozen at their hole-centered positions. The Yb ionization energies are $E_{ion}=55.29$ and 50.68 eV for ideal Yb_3C_{60} and unrelaxed $Yb_{2.75}C_{60}$, respectively.[15,17] The excess 0.25 Yb atoms in the latter are condensed into Yb metal, giving a cohesive energy

gain $E_{coh}=-0.4$ eV.[18] The total electron affinity in Yb_3C_{60} is approximated as six times the first electron affinity for C_{60} (Ref. 19) plus the electronic self-energy, which is modeled as the minimum energy of six classical point electrons on a uniform spherical shell of radius 3.5 Å;[20] the result is a net energy cost $E_{ea}=-15.90+41.04=25.14$ eV. The analogous energy for transferring 5.5 electrons to C_{60} in $Yb_{2.75}C_{60}$ 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 $E_{ea}=-14.58+33.17=18.59$ eV. Finally, the ions are assembled into their fcc-based structures, giving Madelung energies $E_{Mad}=-91.43$ eV for Yb_3C_{60} and -77.65 eV for $Yb_{2.75}C_{60}$. Comparing the total formation energy $E_{form}=E_{ion}+E_{coh}+E_{ea}+E_{Mad}=-11.00$ eV for ideal Yb_3C_{60} with $E_{form}=-8.78$ eV for unrelaxed $Yb_{2.75}C_{60}$ shows that the larger Madelung energy gain in forming Yb_3C_{60} exceeds its larger ionization and self-energy costs, and thus creating T-site vacancies in unrelaxed $Yb_{2.75}C_{60}$ is endothermic: $\Delta E_{form}=2.22$ 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, viz., 2.41 Å.[12] 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 $E_{displ}=-2.40$ eV.

The above calculations assumed that the charges on all C_{60} anions are given by the average number of electrons per C_{60}, i.e., $-5.5e$.[15] The crystallographic inequivalence of the anions [see Fig. 1(c)], however, makes favorable the prospect[14] of transferring electrons from C_{60} (1), with 12 NN cations, to C_{60} (3), which has only 8. We investigate this possibility by allowing the inequivalent C_{60} (1), C_{60} (2), and 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 $E_{Mad}+E_{ea}$ with respect to q_i gives $q_1=6.3$, $q_2=5.5$ and $q_3=4.7$. The charge of C_{60} (2) is unchanged, while $0.8e^{-}$ is indeed transferred from C_{60} (3) to C_{60} (1), confirming the predictions of Ref. 14 and roughly consistent with the vacancy-potential screening by intermolecular charge transfer in Ref. 11. We calculate the energy associated with this charge redistribution process,[21] $E_{redistr}$, to be just -0.17 eV (reflecting the nonlinear self-energy of electrons on C_{60}). Adding $E_{redistr}$ to E_{displ} gives a relaxation energy gain of -2.57 eV, which is essentially equal (within the estimated accuracy of our calculations) to $\Delta E_{form}=2.22$ 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,[22,23] and the neighboring Yb^{2+} cations. To calculate
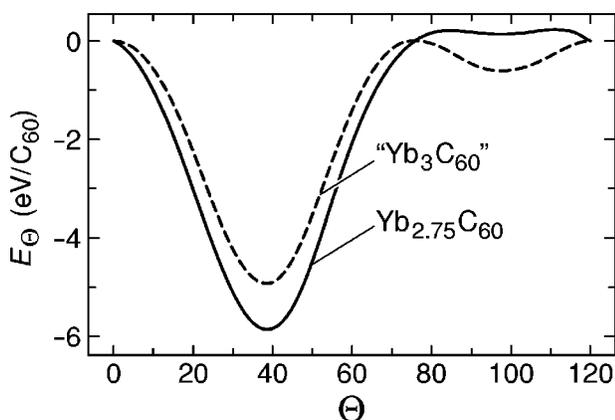
FIG. 2. Angular dependence of orientational interaction energy in the $Yb_{2.75}C_{60}$ and ideal Yb_3C_{60} structures due to rigid rotation of all C_{60} anions about local {111} axes.

this orientational interaction energy obviously requires going beyond approximating the C_{60} anions as uniformly charged spherical shells. Based on comparisons with chemical analogs[14,22,23] and first-principles calculations of C_{60}^{6-},[24] 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.[25] 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 observed in $(Ba^{2+})_3C_{60}^{6-}$ (Ref. 26) and was found to be an important component in achieving the best Rietveld refinement of the $Yb_{2.75}C_{60}$ structure.[12,27]

The orientational interaction energy, E_Θ, was investigated using the set of {111} axes established in the x-ray structural determination;[12] these axes are shown in Fig. 1(c). Each C_{60} anion is rotated by the same angle Θ around its own local axis. Θ is taken to be zero in the uniform reference configuration where the twofold axes of the C_{60} anion are aligned along the Cartesian axes.[28] As shown in Fig. 2, E_Θ for both Yb_3C_{60} and $Yb_{2.75}C_{60}$ depends strongly on Θ and exhibits a pronounced minimum at $\Theta = 37.5°$, consistent with the x-ray refinement results.[12,27] However, because of the large displacements of the O-site cation in $Yb_{2.75}C_{60}$, a greater degree of pentagon-cation interaction is achieved, resulting in an appreciable energy gain relative to ideal Yb_3C_{60}: $\Delta E_\Theta = -0.97$ eV. While we expect our simple point-charge model for distributing charge on C_{60} to overestimate the *absolute magnitude* of the orientational dependence of the energy, the scale of the calculated *difference* ΔE_Θ is meaningful, thereby demonstrating the importance of this effect for stabilizing the observed vacancy-ordered phase.

For completeness, we consider the small relaxation energy that can arise from distorting the C_{60} anions. Even a symmetrically shaped C_{60} anion with a uniform charge distribution will be distorted by the anisotropic crystal field of NN Yb cations [see Fig. 1(c)], and such distortions will be still greater when the C_{60} anion charge distribution is itself anisotropic.[14,22–24] Indeed, recent x-ray absorption and Ra-

man measurements in $Yb_{2.75}C_{60}$ show clear evidence for significant shape deformations of the C_{60} anions.[14] We calculate the relative distortion-energy gain $\Delta E_{distort}$ using the same point-charge model as in the calculation of E_Θ, with the charges allowed to move radially relative to their ideal positions in the $\Theta = 37.5°$ orientation. The stiffness of the C_{60} anion is modeled by connecting the charges to the anion center with harmonic springs whose spring constant is chosen to reproduce the observed $A_g(1)$ radial breathing mode frequency of ~ 500 cm^{-1}.[29] The associated relaxation-energy gain is -0.32 eV in $Yb_{2.75}C_{60}$ and -0.28 eV in Yb_3C_{60}, giving $\Delta E_{distort} = -0.04$ eV. The outward displacements of charge (ranging from 0.01 to 0.04 Å) are somewhat smaller than the C-atom displacements inferred from the x-ray absorption data,[14] suggesting that our model underestimates the absolute distortion energies. Regardless of this underestimation, however, the scale of the difference $\Delta E_{distort}$ is small, indicating that the distortion contribution to the total relaxation energy is small as well.

Our study of the formation and stability of $Yb_{2.75}C_{60}$ reveals the central role played by vacancy-induced structural relaxations. The underlying mechanism responsible for these relaxations is the strong interaction between the anisotropically arranged divalent Yb cations and the anisotropically distributed charge on the C_{60} anions. As shown here, this interaction can be investigated through a relatively straightforward analysis of electrostatic energies, and does not require invoking any chemical behavior peculiar to Yb. Indeed, the same ordered-vacancy structure has been observed in both Ca- (Ref. 27) and Sm-doped[30] C_{60} compounds. Application of our model in these seemingly unwieldy systems (with 2008-atom unit cells) makes clear the relationship between the long-range-ordered vacancies and the crystallographically inequivalent, orientationally ordered C_{60} anions. A T-site cation vacancy leads to the O-site cation displacements, which in turn amplify the orientational cation-anion interactions. Only *one* T-site vacancy per subcell is needed to induce displacements of *all* cations, making the formation of additional vacancies unfavorable. This naturally explains the observed $Yb_{2.75}C_{60}$ stoichiometry.

Given the unsophisticated nature of our model and the structural complexity of this system, it is appropriate to discuss the validity of such apparently simple findings. From a practical viewpoint, fulleride compounds with symmetry-breaking vacancies (regardless of whether or not they are ordered) impose severe limitations on any theoretical analysis. This means it is very difficult to calculate effects that might be considered indispensable in more quantitative analyses of simpler fullerides,[24] such as orbital splittings of C_{60} energy levels,[11,31] quantum mechanical corrections to the electron charge distribution,[32] electron correlation and screening energies,[11,33] and detailed intramolecular distortion energies.[34] However, because metal-intercalated fullerides are ionic systems,[35,36] we regard these effects as desirable but not essential corrections to the dominant electrostatic energies. It is on this basis that we believe our electrostatic model reliably captures the most important structural energetics associated with the formation of cation vacancies and their attendant local relaxations.

A subject of recent debate has been the question of T-site vacancies and off-center displacements for O-site cations in

several fcc-based alkali fullerides.[3,4,8,10] Our model can be readily rescaled for monovalent fullerides, and doing so clearly shows that the electrostatic force between an O cation and a neighboring T-site vacancy is very large. Therefore, in systems such as Rb_3C_{60}, which do exhibit T-site vacancies,[2] the surrounding O-site cations will definitely undergo off-center displacements towards that vacancy [see Fig. 1(b)], limited only by the constraint of cation size. Such displacements are expected to be more difficult to detect than in $Yb_{2.75}C_{60}$ because of the disordered arrangement of the vacancies. The displacements are also expected to strongly inhibit any vacancy hopping, a process which has been recently proposed[8] and challenged experimentally[10] in

explaining the splitting of T-site NMR lines in Rb_3C_{60}.

In summary, a simple model is used to analyze the structural energetics of the ordered-vacancy compound $Yb_{2.75}C_{60}$. The results provide valuable insights into the structural distortions that are locally induced by tetrahedral cation vacancies, and can be extended to the broader class of alkali-metal and alkaline-earth fullerides for the purpose of complementing current and future experimental studies.

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