EFFECTS OF NONSTOICHIOMETRY IN $A_{3-x}C_{60}$ ($A=K, RB$)

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ABSTRACT

We perform self-consistent Hartree calculations for a model of $A_{3-x}C_{60}$ ($A=K, RB$) to study the effects of the presence of vacancies. We find that the strong vacancy potential is very efficiently screened and that the density of states is only weakly influenced by the presence of vacancies.

I. INTRODUCTION

The $A_{3}C_{60}$ ($A=K, Rb$) compounds with the nominal stoichiometry three are believed to actually have the composition $A_{3-x}C_{60}$, with $x \sim 0.07$ [1]. The alkali atoms are believed to be almost completely ionized, and the electrostatic potential from the alkali ions should therefore be large. The presence of a vacancy may then be a large perturbation on the electronic structure. For instance, if a vacancy were completely unscreened, its potential at the centre of a neighboring $C_{60}$ molecule would be about $2.3$ eV and it would split the $t_{1u}$ states by about $0.2$ eV, which is comparable to the $t_{1u}$ band width ($\sim 1/2$ eV) for a system without vacancies. The vacancies occur on the tetrahedral positions [1] and each vacancy is surrounded by four $C_{60}$ molecules. If $x = 0.07$, more than a quarter of the $C_{60}$ molecules have an alkali nearest neighbor vacancy. It is an interesting question how this influences the electronic structure [2].

Similar questions arise for the systems $Na_{2}Cs_{x}C_{60}$ and $K_{3-x}Ba_{x}C_{60}$ [3], which also have different charges at the alkali positions.

We perform Hartree calculations for a model of $A_{3-x}C_{60}$. The model includes the 60 “radial” $2p$ orbitals on each $C_{60}$ molecule, which are allowed to screen the potential from the alkali ions self-consistently. We find that the screening is very efficient, in particular in terms of charge transfer between the molecules and to a less extent in terms of polarizing the molecules. As a result the density of states is almost unchanged by the presence of the vacancies.

In Sec. II we present the model, in Sec. III the method for performing the calculations. The results are given in Sec. IV and some implications are discussed in Sec. V.

II. MODEL

We introduce a model of $A_{3-x}C_{60}$ for which we calculate the electronic structure and the screening properties. For each carbon atom in each molecule we include the $2p$ orbital, pointing radially out from the molecule. The states close to the Fermi energy are mainly formed from these radial $2p$ orbitals, and they are therefore par-
particularly important for the screening. The \( \sigma \)-like 2\( p \) orbitals pointing tangentially to the molecular surface and the 2\( s \) orbitals contribute mainly to orbitals far away from the Fermi energy and are therefore less important. If these orbitals had nevertheless been included, the result would have been an even more efficient screening than found below. Thus we consider the one-particle Hamiltonian

\[
H^0 = \sum_{i\nu} \varepsilon_0 n_{i\nu} + \sum_{i\nu,j\mu} [t(i\nu,j\mu) \psi_{i\nu\sigma}^\dagger \psi_{j\mu\sigma} + \text{h.c.}],
\]

where \( \varepsilon_0 \) gives the energy of the 2\( p \) states and \( t(i\nu,j\mu) \) gives the hopping integrals between these states. The atoms in a \( \text{C}_60 \) molecule are labelled by Roman letters and the \( \text{C}_60 \) molecules are labelled by Greek letters. This includes both hopping within a molecule and hopping between states on nearest neighbor molecules. We have used the parametrization in Ref. \[4\], but multiplied all hopping integrals by a factor 1.2 to obtain a \( t_{1u} \) band width in agreement with recent band structure calculations. The \( \text{C}_60 \) molecules have an orientational disorder, and take essentially randomly one out of two preferred directions\[5\]. This is built into the hopping matrix elements\[6\].

The Coulomb integrals between the orbitals are defined as

\[
v(i\nu,j\mu;\nu\gamma,n\delta) = \int d^3r d^3r' \phi(r - R_{i\nu})\phi(r - R_{j\mu}) \frac{e^2}{|r - r'|} \phi(r' - R_{\nu\gamma})\phi(r' - R_{n\delta}),
\]

where \( R_{i\nu} \) is the position of the \( i \)th atom on the \( \nu \)th \( \text{C}_60 \) molecule. We neglect the overlap of the functions centred on different atoms, and therefore \( v \) is nonzero only if \( (i\nu) = (j\mu) \) and \( (\nu\gamma) = (n\delta) \). We make the assumption

\[
v(i\nu,j\mu;\nu\gamma,n\delta) = \delta_{i,j}\delta_{\nu,\mu}\delta_{\nu,\mu}\delta_{\gamma,\delta} \left\{ \begin{array}{ll}
\frac{e^2}{|R_{i\nu} - R_{\nu\gamma}|} & \text{for } |R_{i\nu} - R_{\nu\gamma}| > 0 \\
v_0 & \text{for } |R_{i\nu} - R_{\nu\gamma}| = 0
\end{array} \right.
\]

For the on-site interaction, we have obtained \( v_0 = 12 \) eV from atomic calculations.\[7\] For the Coulomb integrals between an alkali core and the carbon 2\( p \) orbitals a similar expression is used.

The \( \text{C}_60 \) molecules are put on a fcc lattice with the lattice parameter 14.24 Å, and the alkali atoms are placed on the octahedral and tetrahedral positions. It was assumed that all \( \text{C}_60 \) molecules and alkali ions are at their ideal positions, and that there are no distortions due to the vacancies. We introduce a large supercell with 500 molecules, which is periodically repeated. This supercell is large enough to give results which are essentially converged with respect to the cell size. Within the supercell each \( \text{C}_60 \) molecule is allowed to take one of the two preferred orientations randomly. Furthermore vacancies are introduced randomly on the tetrahedral positions in such a way that on the average there are 3\( - x \) alkali atoms per unit cell. To keep the system neutral, we fill up the \( t_{1u} \) band with exactly as many electrons as there are alkali ions in the system.
III. METHOD

We perform self-consistent Hartree calculations. For strongly correlated systems, this approach might be expected to give poor description of the screening. By comparing Quantum Monte Carlo and RPA calculations, it has, however, been found that RPA remains surprisingly accurate up values of the Coulomb interaction where the Mott-Hubbard transition takes place\cite{8, 3}. Since even stoichiometric A$_3$C$_{60}$ is believed to be on the metallic side of a Mott-Hubbard transition\cite{3}, we expect the Hartree approximation to be qualitatively correct in the present situation.

To study the model described above, we use the molecular solid character of the system. The potential from the vacancies is screened in two ways. First, there is a charge transfer between the molecules to approximately neutralize the alkali vacancies, i.e., molecules which are nearest neighbors to a vacancy have a smaller electronic charge. This screening is very efficient and mainly takes place in the partly filled $t_{1u}$ band. Below we only consider the charge transfer in this band. Second, the molecules polarize so that within a given molecule the charge moves away from a vacancy. Below we assume that the polarization can be calculated by studying an isolated molecule in the potential of the surrounding molecules and alkali ions.

First we calculate the potential for each atom in each molecule due to the the alkali ions and the charges on all other atoms in the C$_{60}$ molecules. In this process we take into account that the “core” of a carbon atom has the charge +1, since the $\sigma$ electrons are counted in the core. This calculation is performed using a Madelung summation technique. For each molecule we then solve the corresponding 60 $\times$ 60 Hamiltonian, to obtain the $\pi$-orbitals. The lowest 30 orbitals are occupied, and the corresponding charges are calculated for the 60 atoms in each molecule. This describes the polarization of the molecules.

To describe the charge transfer between the molecules, we consider the three $t_{1u}$ orbitals on each atom. From the molecular calculations described above, we obtain the energies of the $t_{1u}$ orbitals, which in general are not degenerate due to the random arrangement of the alkali vacancies. These energies give the diagonal elements in a $3N \times 3N$ matrix, where $N$ is the number of molecules in the unit cell. From the calculated coefficients of the $t_{1u}$ orbitals and the hopping integrals between $2p$ orbitals on different molecules, we obtain the hopping matrix elements between $t_{1u}$ orbitals on different molecules. These give the nondiagonal matrix elements in the $3N \times 3N$ Hamiltonian matrix. We use periodic boundary conditions when setting up the hopping part of the matrix, which corresponds to considering the $k = 0$ solution. Due to the large size of the supercell and the corresponding small size of the Brillouin zone, this should be a good approximation. Finally, we diagonalize the $3N \times 3N$ matrix and obtain the $t_{1u}$ contribution to the charge density.
IV. RESULTS

The results for the density of states $N(\varepsilon)$ are shown in Fig. 1. Some small wiggles in $N(\varepsilon)$ are due to the finite cell size (500 molecules). This does not, however, influence the conclusions. The main result of Fig. 1 is that $N(\varepsilon)$ is practically identical for $x = 0$ and $x = 0.07$. This small difference is due to the efficient screening of the alkali vacancies.

To discuss the screening we introduce the average position

$$\varepsilon_{t_{1u}}(i) = \frac{1}{3} \sum_{m=1}^{3} \varepsilon_{t_{1u}}(im),$$

and standard deviation

$$\sigma_{t_{1u}}(i)^2 = \frac{1}{3} \sum_{m=1}^{3} (\varepsilon_{t_{1u}}(im) - \varepsilon_{t_{1u}}(i))^2,$$

of the $t_{1u}$ level, where $\varepsilon_{t_{1u}}(im)$ is the energy of the $m$th orbital on the $i$th molecule. We also introduce the average of this standard deviation

$$\sigma_{t_{1u}} = \frac{1}{N} \sum_{i=1}^{N} \sigma(i).$$

$\sigma(i)_{t_{1u}}$ and $\sigma_{t_{1u}}$ measure how the degeneracy of the $t_{1u}$ orbitals is lifted due to the random positions of the vacancies. It is also interesting to see how the average $t_{1u}$ position varies between the sites. For this purpose we introduce the standard deviation

$$\Delta_{t_{1u}}^2 = \frac{1}{N} \sum_{i=1}^{N} (\varepsilon_{t_{1u}}(i) - \bar{\varepsilon}_{t_{1u}})^2,$$

where $\bar{\varepsilon}_{t_{1u}}$ is the average of the $t_{1u}$ energies over the super cell. In a similar way we define $\Delta_{tetra}$ and $\Delta_{oct}$ as the standard deviation in the potentials at the occupied tetrahedra and octahedral positions, respectively.
Table 1: On-site splitting $\sigma_{t_{1u}}$ (Eq. (6)) and off-site splitting $\Delta_{t_{1u}}$ (Eq. (7)) of the $t_{1u}$ level as well as the splitting in the potential on the tetrahedral ($\Delta_{tetra}$) and octahedral ($\Delta_{oct}$) occupied positions for $A_{3-x}C_{60}$. The first three lines refer to the system without vacancies ($x = 0$) and the following three lines to a system with 7% ($x = 0.07$). The band width $W$ is also shown. All energies are in eV.

|              | $x$ | $\sigma_{t_{1u}}$ | $\Delta_{t_{1u}}$ | $\Delta_{tetra}$ | $\Delta_{oct}$ | $W$ |
|--------------|-----|------------------|-------------------|------------------|----------------|-----|
| Nonself-consistent | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.53 |
| $t_{1u}$ self-consistent | 0.0 | 0.00 | 0.01 | 0.01 | 0.01 | 0.54 |
| Self-consistent | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | 0.55 |
| Nonself-consistent | 0.07 | 0.31 | 6.83 | 6.76 | 6.72 | 32.31 |
| $t_{1u}$ self-consistent | 0.07 | 0.01 | 0.04 | 0.08 | 0.20 | 0.71 |
| Self-consistent | 0.07 | 0.01 | 0.02 | 0.01 | 0.05 | 0.55 |

As discussed above, there are two types of screening. Due to rearrangements of the partly occupied $t_{1u}$ band, charge is transferred between the molecules. This influences the averaged positions $\varepsilon_{t_{1u}}(i)$ of the $t_{1u}$ level on the different molecules, and it therefore reduces $\Delta_{t_{1u}}$. This also reduces the splitting of the $t_{1u}$ levels inside a molecule. This splitting is further reduced by rearrangements of the charge inside the molecules.

We therefore perform three types of calculations. First, we perform a nonself-consistent calculation, where only the potentials from the alkali ions are considered, and any screening from the $C_{60}$ molecules is neglected. Second, we perform a calculation where charge transfer between the molecules is allowed, but polarization of the $C_{60}$ molecules is neglected ($t_{1u}$ self-consistent). Finally, we perform the full self-consistent calculation as discussed above. The results are summarized in Table 1.

In the nonself-consistent calculation, we find a very large variation ($\Delta_{t_{1u}}$) in the average position of the $t_{1u}$ level between different molecules for $x = 0.07$. There is also a large splitting ($\sigma_{t_{1u}}$) of the $t_{1u}$ level on molecules close to a vacancy. As a result the band width $W$ is huge. When charge transfer between the molecules is allowed ($t_{1u}$ self-consistency) the variation in the $t_{1u}$ level position between the molecules becomes very small. In the fully self-consistent calculation, the polarization of the molecules reduces the splitting of the $t_{1u}$ level somewhat more. Thus the largest value of $\sigma_{t_{1u}}(i)$ is reduced by about a factor of four and the average value by about a factor of two. Due to the rounding in Table 1, this is not seen explicitly. Similar results are found for the potential on the alkali ion positions, and the potential on the different occupied tetrahedral sites only varies by a few hundredths of an eV.
V. CONCLUDING REMARKS

We find that the strong potential from an alkali vacancy is efficiently screened by charge transfer between the molecules and to some extent also by polarization of the molecules. As a result, the density of states $N(\varepsilon)$ is hardly influenced by the vacancies. These results were obtained under the assumption that there are no distortions of the C$_{60}$ molecules and alkali ions around the vacancies.

One might have expected that the strong vacancy potential would lift the $t_{1u}$ degeneracy on a given molecule, thereby increasing the band width with vacancy concentration. This would have reduce $N(0)$ and the electron-phonon interaction $\lambda$, and it might have explained the rapid drop$^3$ in $T_c$ as the stoichiometry deviates from three. Due to the efficient screening found above, such an explanation, however, seems unlikely.

In NMR of Rb$_{3-x}$C$_{60}$ ($x \sim 0.03$) it is found that the quadrupolar distortion of the Rb lines is rather small, in spite of the electric field gradients one would expect from the vacancies$^{10}$. It was argued that this may be due due to an efficient screening of the vacancies$^{10}$. Such considerations agree very well with the present results.

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