Electron energy-loss studies of \( \text{Na}_x \text{C}_{60} \) compounds

J.F. Armbruster\(^1\), M. Knupfer\(^2\), J. Fink\(^2\)

\(^1\)Forschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, Postfach 3640, D-76021 Karlsruhe, Germany
\(^2\)Institut für Festkörper- und Werkstoffforschung, Postfach 270016, D-01171 Dresden, Germany

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Abstract. The crystal and electronic structure of \( \text{Na}_x \text{C}_{60} \) (4 \( < x < 10 \)) has been investigated using electron energy-loss spectroscopy in transmission. Electron scattering experiments confirm that the crystal symmetry remains face centered cubic over the entire intercalation range. The electronic structure shows a close similarity for the \( \text{Na}_x \text{C}_{60} \) and \( \text{Na}_4 \text{C}_{60} \) compounds compared to the corresponding K and Rb systems. Upon intercalation to higher stoichiometries up to \( \text{Na}_{10} \text{C}_{60} \) the charge transfer from sodium to \( \text{C}_{60} \) turns out to be incomplete, something that has never been observed before in alkali intercalated systems. Current theoretical calculations indicate that this can be understood by taking into account additional states related to the Na atoms in the octahedral site. In \( \text{Na}_{10} \text{C}_{60} \) the partial filling of the \( t_{1u} \) level of \( \text{C}_{60} \) leads to additional electronic transitions near the Fermi energy.

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Introduction

The superconducting properties of intercalated fullerenes have induced many investigations of the crystal and electronic structure of this new class of materials. For the alkali metal intercalated fullerenes the intercalation range up to 6 has been studied intensively [1]. In contrast to the K, Rb, and Cs systems, where the maximum stoichiometry is \( \text{A}_x \text{C}_{60} \) (\( \text{A} = \text{K}, \text{Rb}, \text{Cs} \)), x-ray diffraction studies of \( \text{C}_{60} \) intercalated with Na revealed that intercalation up to about 10 could be achieved and that \( \text{Na}_x \text{C}_{60} \) behaves like a solid solution [2]. While these studies show that the crystal structure of \( \text{Na}_x \text{C}_{60} \) remains face centered cubic (fcc) over the entire intercalation range, the electronic structure of the samples is still unclear. From the alkaline-earth fullerenides it is known that a charge transfer not only into the \( t_{1u} \) but also into the \( t_{1g} \) derived states is possible [3–7], also resulting in metallic and superconducting compounds [1]. In addition, photoemission and electron energy-loss spectroscopy (EELS) investigations \([8, 9]\) on \( \text{C}_{60} \) molecules deposited on alkali metal surfaces reveal doping levels up to 12, i.e., a complete filling of the \( t_{1g} \) band.

In this paper we report on studies of thin crystalline \( \text{Na}_x \text{C}_{60} \) films with intercalation levels in the range of 4 \( \leq x \leq 10 \). Electron diffraction measurements revealed the lattice constants and thus, from comparison with [2] and [10], the intercalation levels of the samples could be derived. The electronic structure measured by EELS of the \( \text{Na}_x \text{C}_{60} \) and \( \text{Na}_4 \text{C}_{60} \) samples is compared directly with that of the corresponding K, Rb, and Cs stoichiometries. For the higher intercalated samples above \( \text{Na}_x \text{C}_{60} \) theoretical calculations [18] predict additional states below the \( t_{1u} \) bands of \( \text{C}_{60} \). To test these predictions we studied the Na2p and the C1s core level excitations for the entire intercalation range, which reveal the charge of the Na ions and the \( \text{C}_{60} \) molecules, respectively. Measurements of the low-energy loss function are used to investigate the transitions near the Fermi energy.

Experimental

Thin films of pure \( \text{C}_{60} \) were prepared by evaporation of \( \text{C}_{60} \) onto KBr single crystals under ultra-high vacuum (UHV) conditions. From previous transmission electron microscopy measurements [11] we know that this procedure yields samples with an average grain size of about 1000 Å. The film thickness was about 1000–1500 Å. These films were floated off in distilled water and mounted onto standard electron microscopy grids. After transferring them into the EELS spectrometer the films were annealed in situ at 570 K for 30 minutes under UHV conditions to remove possible contaminations from the substrate or from the floating process. Subsequent characterization with EELS and electron diffraction did not show any contamination after sample annealing.

Pure sodium was deposited onto these films from carefully degassed commercial getter sources (SAES) under UHV conditions until a composition of \( \text{Na}_x \text{C}_{60} \) was achieved. Subsequently, the samples were annealed at various temperatures and for times from 370 K and 10...
Fig. 1. Electron diffraction spectra of Na$_x$C$_{60}$ in the range of 4 ≤ x ≤ 10. The curves are labelled by the intercalation level x. The reflections expected for a fcc lattice with the lattice constant of 14.59 Å are indicated by the ticks above the bottom axis.

The intercalation levels could be confirmed by the Na2p absorption edges shown in Fig. 2. These features are situated on the high energy side of the σ + π plasmon [14]. The sodium content was determined from the area of the peak at ∼ 33 eV and from its associated edge jump. However, this method is not as accurate as the lattice constant measurements due to uncertainties in back-ground subtraction.

The electron diffraction and EELS measurements in transmission were performed in a spectrometer with a primary energy of 170 keV and a base pressure of 5 × 10$^{-10}$ mbar. Details of the spectrometer are given elsewhere [15]. The energy and momentum resolution was 110 meV and 0.03 Å$^{-1}$ for elastic electron scattering experiments and measurements of the loss function at low energies and 140 meV and 0.2 Å$^{-1}$ for the core level excitations, respectively. The low-energy loss spectra have been corrected for quasi-elastic line contributions. We

FIGURE 1: Electron diffraction spectra of Na$_x$C$_{60}$ in the range of 4 ≤ x ≤ 10. The curves are labelled by the intercalation level x. The reflections expected for a fcc lattice with the lattice constant of 14.59 Å are indicated by the ticks above the bottom axis.

FIGURE 2: Na2p absorption edges of Na$_x$C$_{60}$ in the range of 4 ≤ x ≤ 10. The curves are labelled with the intercalation level x.