

# MOMENTUM DENSITY IN $K_xC_{60}$

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## Introduction

$K_xC_{60}$  systems, with  $x$  taking values of 1, 3, 4 and 6, have attracted the attention of many authors. *Ab initio* SCF energy band calculations have shown the important role played by the three unoccupied  $t_{1u}$  bands of solid  $C_{60}$ . The total charge transfer of the originally  $s$  electron of potassium to the  $C_{60}$  ball explains, in particular, the insulating behavior of  $K_6C_{60}$ , with filled  $t_{1u}$  bands, and the metallic behavior of  $K_3C_{60}$ , with only half filled  $t_{1u}$  bands.  $K_4C_{60}$  has an insulator behavior, unexpected by both the "rigid band model" and our SCF calculations. A strong distortion of electronic density of the  $C_{60}$  host, due to alkali ions, can play an important role.

Since most of the theoretical studies of electronic structure of  $K_xC_{60}$  have been carried out using the density-functional-theory and the local-density-approximation (LDA),<sup>1-3</sup> it is important to test the applicability of these approaches, as well as the quality of the specific calculation, by a direct experimental test of the ground-state charge density. Compton scattering measurements have been shown to provide such a probe, especially for the related graphite based compounds.<sup>4,5</sup> Two important reasons lead to choice of Compton scattering for investigation of synthetic materials: first, it is a bulk measurement and second, due to incoherent nature of the process, it is insensitive to defects in solids.

In this work, we have carried out a combined experimental and theoretical investigation of solid  $K_xC_{60}$  as well as for  $C_{60}$  as a reference material.

## Method

Compton scattering involves the inelastic scattering of photons by electrons. The conservations of energy and momentum lead to a relationship between the energy lost

by the photon and the projection of the initial electron momentum along the scattering vector  $\mathbf{K}$ . The component of energy loss which results from scattering by electrons at rest is referred to as the Compton shift. The motion of electrons in the system results in a Doppler broadening of the distribution around the Compton shift and is a direct indicator of their initial momentum distribution.<sup>6,7</sup> Directional Compton profile (DCP) for the valence electrons can be written as:

$$J(p_z) = \int n(\mathbf{p}) dp_x dp_y = J(q)$$

where  $n(\mathbf{p})$  is the electron density obtained from the wavefunction  $\chi(\mathbf{p})$  and  $q=p_z$  is the projection of electron momentum on the scattering direction.

In addition, inelastic scattering measurements are the unique method to study electron-electron correlations in solids<sup>8</sup> and this is important to study in this serie of compounds, one of them ( $x=3$ ) having a super conducting behavior.

## Experiment

Compton profiles were measured on powder  $K_xC_{60}$  samples, with  $x$  taking values of 1, 3, 4 and 6, using the focusing high resolution spectrometer<sup>9</sup> at LURE (French Synchrotron Facility, Orsay). Synchrotron radiation beam is monochromatized to select 16 keV photons. The resolution function is 0.16 a.u. of momentum. The samples have been kept under dry argon all the time. For comparison, directional Compton profiles have been measured on powder  $C_{60}$  at room temperature.

## Theory

*Ab initio*, all-electron SCF energy band structure calculations were carried out within the local density approximation using the LCAO method with a Gaussian

basis.<sup>10,11</sup> The ground-state wave functions were then expanded in plane waves to be used in the calculation of directional Compton profiles. Each (DCP) is obtained by the summation over the 120 occupied valence bands of crystalline C<sub>60</sub>.<sup>12</sup> The large size of the unit cell in real space leads to a very small Brillouin zone (BZ), thus a mesh of 11 **k** points in the irreducible sector (1/24) of the BZ was sufficient for accurate integration. On the other hand, the number of **G**'s (reciprocal lattice vectors) required to achieve convergence is related to the size of the primitive unit cell and also increases with the hardness of pseudopotentials. Since the magnitudes of the reciprocal lattice vectors were very small here, it was necessary to keep 64 000 components in the sum over **G** in order to achieve convergence. Theoretical DCP were averaged for comparison with the powder measurements.

## Results and Discussion

Due to the flatness of the core profile in momentum space, it is easy to subtract its contribution, evaluated using the Quasi-Self-Consistent-Method, from the measured profile, i.e. the total profile. As a result, the deduced profile is due to the valence electrons and conduction electrons, if any, alone.<sup>13,14</sup> All the outer electron profiles (valence and conduction) are normalized to the number of outer electron for a carbon atom i.e. 4, in case of C<sub>60</sub> and to 4 + x/60, in case of the intercalated compounds.

For each value of x, experimental and theoretical difference between the K<sub>x</sub>C<sub>60</sub> powder profile and the C<sub>60</sub> profile are used and compared. An advantage of this representation is that the effects of the systematic errors are canceled out in both theory and experiment, leading to an accurate picture of electron density in the solids.

We have already observed the narrowness of the C<sub>60</sub> powder profile with respect to graphite profile, interpreted as a larger delocalisation of valence electrons in C<sub>60</sub> than in graphite,<sup>15</sup> assuming that this delocalisation is mainly a molecular effect

In case of intercalated compounds, experimental difference between K<sub>x</sub>C<sub>60</sub> and C<sub>60</sub> DCP is due, for each x value, to potassium insertion effects:

- i- charge transfer of the initially *s* electron of K to the C<sub>60</sub> molecule,
- ii- presence of the initially 3 *p* electrons of K, hybridized with the carbon electrons
- iii- distortion of the C<sub>60</sub> electron density, due to the presence of the K ion and to the structural transition, if any.

The experimental differences were compared with the theoretical differences, obtained from our calculations, in order to investigate the distortion of C<sub>60</sub> charge distribution as a function of x.

In conclusion, we have evidenced large distortions of the electronic density of the host C<sub>60</sub>: this difference is positive for low impulsion values and negative for  $p_z > 2$  a.u.. This phenomenon suggests that the delocalisation of the host C<sub>60</sub> electrons in K<sub>x</sub>C<sub>60</sub> systems is larger than the already measured in C<sub>60</sub> solid. Moreover, we have noticed that K<sub>3</sub>C<sub>60</sub> Compton profile is clearly broader, in the impulsion space, than K<sub>4</sub>C<sub>60</sub> and K<sub>6</sub>C<sub>60</sub>'s profiles. We have to notice that these two compounds are both insulators. Such strong distortions are due to "solid-state effects" and understanding their nature means to clarify the nature of the electronic properties of these materials.

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