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Solid State Effects in C_{60} Fullerite

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The fingerprint of a small but significant solid state effect has been observed in the energy dispersion of the angle-resolved electron distribution curves of the valence band derived from the highest-occupied molecular orbital of C_{60}. The measurements were performed on heteroepitaxial films of C_{60} on GeS(001). We point out that because of the small size of the surface-Brillouin zone of C_{60} this effect can be revealed only at very low excitation energies below 10 eV. The observed dispersion of 400 meV is in reasonable agreement with recent calculations including orientational disorder.

1. Introduction

C_{60} has been recently discovered as the third allotropic form of carbon. Unlike the other condensed forms of carbon, i.e. graphite and diamond, solid C_{60} (fullerite) is a molecular solid, mainly determined by van der Waals bonding between individual molecular clusters. Indeed, the first photoemission experiments carried out on the electronic structure of solid C_{60} revealed many molecular features reproducing closely those of isolated clusters measured in the gas phase [1]. This is especially true for the highest occupied molecular orbital (HOMO) feature corresponding to the H_u or $l = 5$ π-derived state according to a classification assuming for C_{60} a spherical symmetry. In the solid phase, the Pauli repulsion shall disperse this energy level into an electronic band whose width is directly related to the overlap of the molecular orbitals (MO), and thus to the electron hopping probability between adjacent C_{60} molecules. Due to the small MO overlap, band structure calculations estimate in the case of solid C_{60}, an average energy dispersion not higher than 500 meV [2, 3].

In a recent paper devoted to the electronic structure of C_{60}, Wu et al. addressed specifically the issue of the intrinsic band width of the HOMO-derived state, which could be an important piece of information for the understanding of the superconductivity observed in the doped fullerenes. From angle-resolved photoemission measurements performed on a small C_{60} single crystal at different excitation energies, they concluded that the HOMO derived band does not disperse significantly (less than 50 meV) and that its photoemission peak is mainly dominated by Franck-Condon broadening. We note that in the

angle-resolved photoemission experiments reported by Wu et al., very small size single crystals were oriented by Laue diffraction, cleaved in ultra high vacuum (UHV) and that no surface sensitive crystallographic technique was used *in situ*.

It is obvious that high quality large single crystals with well defined crystallographic orientations are needed if one wants to measure dispersion effects as small as 0.5 eV. The originality of our approach consists of using epitaxial films of C_{60} instead of single crystals. Indeed, Van der Waals epitaxy of C_{60} has been successfully demonstrated in our laboratory, on various substrates [5], and especially on a lamellar semiconductor substrate GeS(001) [6]. In this latter case, the heteroepitaxial growth is favored by a one-dimensional commensurability between adsorbate and substrate and also by the natural corrugation exhibited by the GeS(001) cleaved surface. The outstanding purity and crystallography of the as-grown $C_{60}(111)$ surfaces were checked by low energy electron diffraction (LEED) and also by angle-resolved inverse photoemission [6] (ARIPES) which is known to be very sensitive to surface defects and contaminations.

2. Experimental details

A first series of angle-resolved photoemission experiments [7] was conducted on the high resolution SU3 beamline of the SUPERACO storage ring at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE, Orsay). The GeS single crystal surface (6x6 mm^2) was prepared by cleavage in UHV. The fullerene powder, received from G. Sawatzky (University of Groningen), was loaded in the graphite crucible of a standard Knudsen effusion cell (W/A Technology). C_{60} was then sublimed and deposited on the GeS(001) substrate held at 500 K. The film thickness which was monitored by a quartz crystal oscillator, was set to a value of about 120 Å, thick enough to suppress any contribution from the substrate and from the interface, but thin enough to avoid charging effects. Sharp hexagonal LEED patterns were observed, corresponding to the face-centered cubic structure of $C_{60}(111)$. Electron distribution curves (EDC's) of the valence bands were recorded along the $\overline{\Gamma} - \overline{K} - \overline{M}$ direction of the surface Brillouin zone (SBZ) with a photon energy of 29 eV.

For reasons that will be explained below, the same experiments [7] were repeated with lower photon energies ($h\nu = 8.1$ eV) on the Seya-Namioka beamline at the Hamburg Synchrotron Radiation Laboratory (HASYLAB, Hamburg, Germany). In both cases, the global energy resolution was of the order of 100 meV and the typical aperture angle of the electron analyzer was $\Delta\theta_a \approx 2°$.

3. Results and discussion

Fig.1 displays, for reference, a typical EDC obtained in our laboratory, on a heteroepitaxial film of C_{60} with an excitation energy of 21 eV (HeI). Such spectra have been extensively described and commented in the literature [8]. As already indicated in the introduction, although the overall width measured for the valence band is almost identical for all three allotropic forms of carbon, sharp molecular states are observed for C_{60}, in contrast to the broad structures presented by graphite and diamond. On the other hand, as pointed out by Lichtenberger et al. [1], the photoionization spectrum of C_{60} in

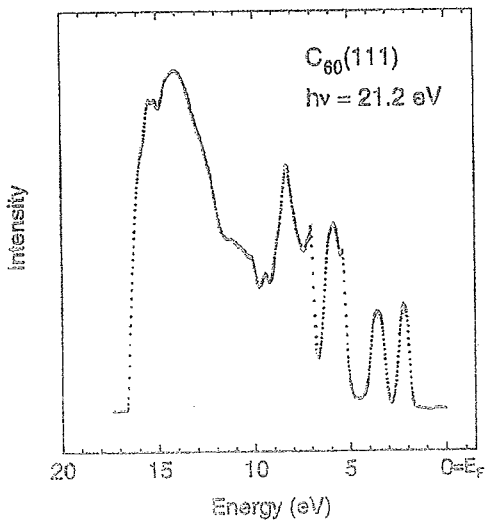

Figure 1. EDC of the valence band of a C_{60} thin film measured with HeI excitation.

thin films, is very similar to gas phase results, as far as the peak widths are concerned. However, as for the condensed phase, some fine vibrational structure can be resolved in the HOMO and HOMO-1 gas phase peaks.

The frontier HOMO orbitals have mainly π-character, while those lying lower in the valence bands have s-character. In keeping with the theoretical analyses of Martins et al. [3], and Saito and Oshiyama [2], the electronic valence band states of C_{60} can be described with the help of spherical harmonics and labeled according to their angular quantum number l, which corresponds to the number of nodes of the orbitals. Consequently, in this framework, the HOMO feature is considered as a π_u state with fivefold degeneracy (l=5).

In the study presented here, we shall concentrate on the HOMO feature. Indeed, elementary solid state considerations predict that dispersion effects should be highest for the least bonded states at the top of the valence band. Fig.2 shows EDC's measured at the LURE storage ring, with a photon energy of 29 eV. Due to transition matrix elements effects, the relative intensities of the different valence bands exhibited drastic changes with excitation energy. The results of Fig.2 were disappointing in the sense that they showed no clear dispersion effect, except for one EDC. Indeed, when comparing closely the spectrum recorded at the $\overline{\Gamma}$ point, with respect to the other spectra, a small shift of the HOMO peak (of the order of 100 meV, i. e. the energy resolution of the experiment) could be observed.

In an angle-resolved photoemission experiment, the electron wavevector component parallel to the surface, $k_{\|}$, is deduced from energy and momentum conservations, assuming a free electron-like state as the final state inside the sample:

$$k_{\|} = 0.51\sqrt{E_i + h\nu - \phi}\,\sin\theta_a \qquad (1)$$

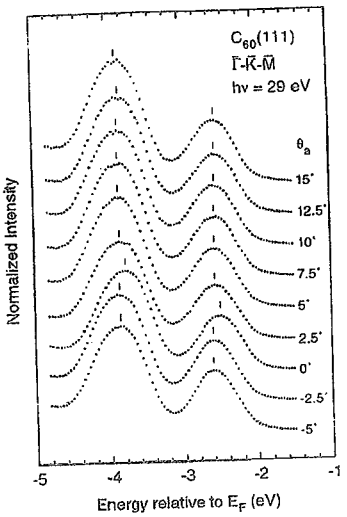

Figure 2. Collection of EDC's of the HOMO and HOMO-1-derived bands of a heteroepitaxial C_{60} thin film measured in the $\overline{\Gamma}$-$\overline{K}$ direction of the SBZ, with 29 eV photon energy.

In equation (1), $k_{\|}$ is in reciprocal Å, E_i is the initial state total energy (in eV), $h\nu$ is the excitation energy, ϕ is the work function of C_{60} (4.7 eV, see below), and θ_a is the angle of analysis. Taking account of an analyzer angular acceptance $\Delta\theta_a = 2°$, the range of wavevectors measured in one single spectrum taken at fixed angle is :

$$\Delta k_{\|} = 0.51\sqrt{E_i + h\nu - \phi}\,\cos\theta_a \Delta\theta_a \tag{2}$$

At a photon energy of 29 eV, and for the HOMO state whose maximum is situated at $E_i = -2.2$ eV, we obtain for the spectrum recorded at normal emission :

$$\Delta k_{\|} = 2.37\Delta\theta_a = 0.084\ \text{Å}^{-1} \tag{3}$$

This wavevector resolution is to be compared to the reciprocal length of the surface Brillouin zone (SBZ), which in the present direction of analysis ($\overline{\Gamma} - \overline{K}$) is as small as 0.42 Å^{-1}. Such a small value is an immediate consequence of the large size of the lattice parameter ($d = 14.2$ Å) of fullerite [9], i.e. the crystalline face centered cubic phase of C_{60} at room temperature. Thus, we see that the third EDC of Fig.2, measured at normal emission spans 20 % of the SBZ and that the zone boundary is already reached at the fifth spectrum collecting the electrons emitted at 10°. Owing to the small expected value of the width of the HOMO-derived band, whose dispersion is also mainly concentrated towards the SBZ center [2], it appeared clearly that the experimental conditions at $h\nu = 29$ eV were not favorable to evidence any dispersion effects (if ever present), and that the wavevector resolution had to be significantly improved.

On examining eq.(1), it is obvious that the only degree of freedom available for im-

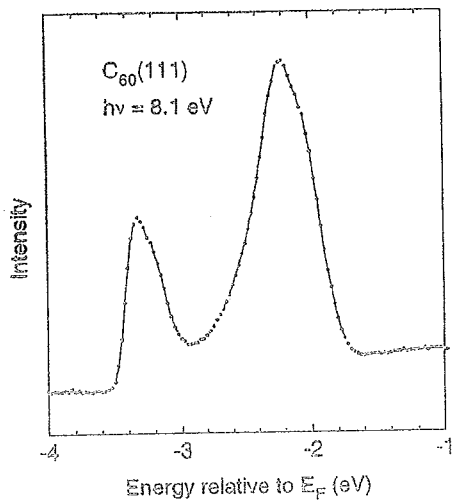

Figure 3. EDC of the valence band of C_{60}, measured in the $\overline{\Gamma}$-$\overline{K}$ direction of the SBZ, with 8.1 eV photon energy, at an emission angle of 7°. The cut-off occurs in the HOMO-1 peak.

proving the $k_{||}$ resolution is the photon energy $h\nu$. This is the reason why a second set of measurements was carried out at the Seya-Namioka beamline station of Hasylab (Hamburg, Germany) where an excitation energy as low as 8.1 eV was available with sufficient intensity. In that case, the photoemission spectrum is drastically squeezed and the secondary cut-off appears very rapidly in the HOMO-1 feature. This notwithstanding, as shown in Fig.3, the HOMO peak, which we are interested in, remained fully contained inside the spectrum. On the other hand, the spectrum of Fig.3 provides a direct determination of the work function of our C_{60} thin films, from the measurement of the cut-off position: the aforementioned value of 4.7 eV was deduced. At a photon energy of 8.1 eV, the wavevector resolution improves considerably to

$$\Delta k_{||} = 0.56\Delta\theta_a = 0.019\text{Å}^{-1} \quad \text{(for normal emission)} \tag{4}$$

Under these conditions, one spectrum averages only over 4% of the $\overline{\Gamma} - \overline{K}$ direction of the SBZ, and the SBZ zone end corresponds to an analysis angle of 48°. Fig.4 displays a collection of EDC's recorded at $h\nu = 8.1$ eV along $\overline{\Gamma} - \overline{K}$. The experimental data show significant angular dependence. In particular, in the spectra of Fig.4, one can immediately identify two features (labeled #2 and #3). Peak #3 is the dominant feature at low emission angles until 15° where it is overcome by peak #2, which was initially observed as a shoulder on the right hand side of peak #3. Peak #2 keeps dominating the spectrum at higher emission angles (not shown here). In order to retrieve the exact number and the precise energy position of the individual bands, we have applied to the data of Fig. 4, a maximum likelihood spectral restoration algorithm (SSRes, from Spectrum Square Associates, Inc.) assuming gaussian lineshapes for each single band. Fig.5 shows

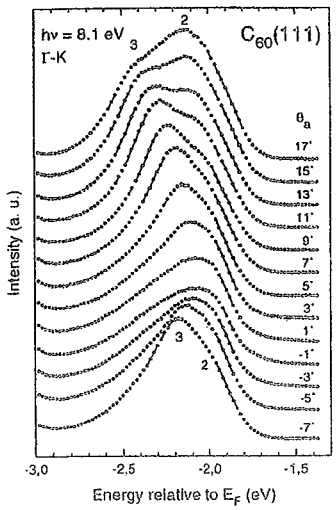

Figure 4. Collection of some EDC's of the HOMO-derived electronic state of C_{60}, recorded for different emission angles in the $\overline{\Gamma}$-$\overline{K}$ direction with a photon energy of 8.1 eV. The position of peaks #2 #3 is indicated.

the result of the filtering procedure. A lower intensity peak #4 is now observed in the left wing of peak #3 and a fourth component (peak #1) is developing at the right side of peak #2. Thus, four distinct peaks emerge clearly, with significant energy dispersions. In order to confirm the energy positions of the four states obtained by this procedure, we checked for all spectra that the photoemission peak could be well fitted by a sum of gaussians centered at these positions (an example of such a fit to the first EDC of Fig.4 is shown on Fig.6, superimposed on the experimental data).

In Fig.7, we have plotted the energy versus $k_{\parallel}$ dispersion curves corresponding to the four peaks observed in the measurements at 8.1 eV photon energy. At the center of the SBZ, there is a degenerate energy level which gradually splits into two separate bands, band #1 corresponding to peak #1 (showing little dispersion), and band #2, associated with peak #2, which in turn exhibits a sizeable dispersion of about 100 meV. This value is truly significant compared to the overall experimental energy resolution of 100 meV. The behavior of bands #3 (peak #3) and #4 (peak #4) is rather peculiar as they seem to follow closely the dispersion of band #2, with energy shifts of 200 and 100 meV, respectively. From this parallel behavior, it could make sense to interpret these latter two bands in terms of phonon side-bands of band #2 and not to consider them as distinct energy bands. However, although the phonon spectrum of C_{60} is well known, from theoretical and experimental points of view, it is not straightforward to identify which vibrations are responsible for these satellite bands. A detailed interpretation is beyond the scope of this experimental work and shall require elaborate calculations of photoemission spectra in which transition matrix elements shall include electron-phonon interactions.

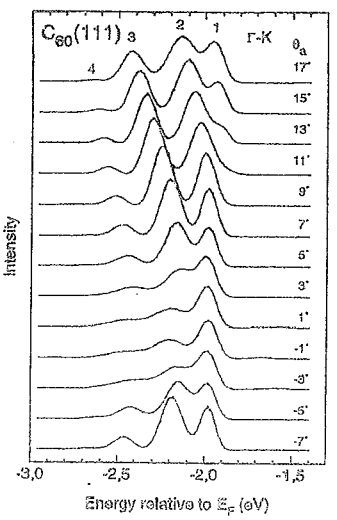

Figure 5. Results of the application of the spectral restoration filter to the EDC's of C_{60} recorded at 8.1 eV photon energy (see text). The dispersion of four peaks is clearly visible.

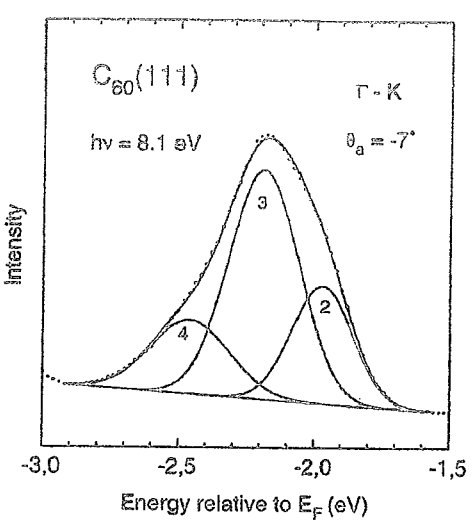

Figure 6. Gaussian fit of the first EDC of Fig.4 from the data of the spectral restoration algorithm.

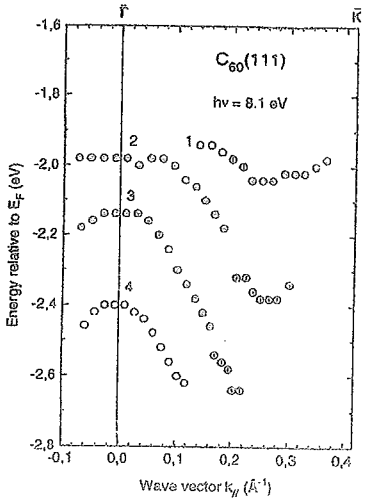

Figure 7. Energy vs. wavevector dispersion curves in the $\bar{\Gamma}$-$\bar{K}$ direction of the SBZ of C_{60} determined from the EDC's measured at 8.1 eV. The filled dots indicate intense peaks, the half-filled dots, medium intensity structures and the open dots represent weak features.

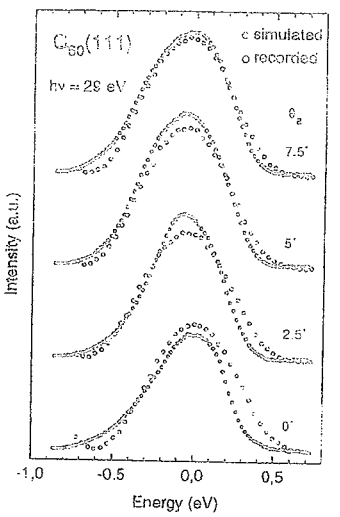

Figure 8. Comparison between the experimental spectra recorded at 29 eV photon energy (open dots) with synthetic spectra obtained by adding up EDC's measured at 8.1 eV (solid dots). The energy scale is relative to the position of the HOMO peak at $\bar{\Gamma}$.