Evidence for bandlike dispersion in K_6C_{60}(110) films

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Using angle resolved photoemission we show that bandlike states in K_6C_{60}(110) films at 40 K survive in spite of the strong electron-phonon coupling expected in fullerides that should give rise to polaron formation. The momentum dependence and the total bandwidth of the dispersing bands contributing to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) features agree quite well with one-electron band structure calculations. While a crude estimation of the dimensionless electron-phonon coupling constant λ, from the temperature dependence of the LUMO linewidth in photoemission spectra, seems to place K_6C_{60} in an intermediate polaronic regime, the expected strong coupling to K^+ modes remains uncertain.

I. INTRODUCTION

The band structure in solid C_{60} compounds is far from being understood due to the experimental and theoretical challenges involved. Orientational disorder, temperature dependent phase transitions, very small Brillouin zone, weak molecular interaction, and strong electron-phonon coupling have combined effects that are difficult (if not impossible) to disentangle and all together imply a level of complexity that, at best, has made difficult the application of theoretical models and the elucidation of experimental results. For example, several calculations[1–4] and recent experiments[5] have demonstrated that band dispersion and bandwidth in C_{60} compounds strongly depend on the molecular orientation. Therefore, it is not obvious that extended electronic states will survive in C_{60} crystals in the presence of the inherent orientational disorder, which may disrupt the band formation or strongly renormalize the bandwidth compared to one-electron band structure calculations. In addition, as vibrational broadening plays a major role in determining the line shape of gas phase photoemission spectral features,[6] we should expect *a priori* a similar significant contribution also in the solid-state spectra. Indeed, the strong similarity between gas-phase and solid C_{60} photoemission spectra seems to support this hypothesis[7] and suggests that polaronic effects may be important in two-dimensional (2D) and three-dimensional (3D) fullerene structures. Brühwiler *et al.*[7] claimed that in C_{60} 2D islands on graphite, vibronic coupling accounts for most of the observed bandwidth, while the band dispersion is reduced to less than 70 meV by polaronic effects. These authors conclude that a similar phenomenon and band dispersion reassessment should persist for the 3D solid.

Conflicting pictures have been obtained for undoped C_{60} crystals and films. The first angle-resolved photoemission experiment on a cleaved C_{60} single crystal[8] showed very little or no band dispersion, indicating the relevant importance of the electron-phonon interaction on the band structure of the solid: The width and shape of the measured valence band photoemission features are dominated by phonon broadening and do not reflect the intrinsic bandwidth. Subsequent angle resolved photoemission experiments[9,10] performed at lower photon energies on C_{60} thick films, were successful in observing intensity modulations and line shape changes in the HOMO and HOMO-1 features, which were interpreted as band dispersion of both occupied and unoccupied (final states) bands. These low energy photoemission experiments were taken as evidence for the existence of bandlike electronic states in fcc C_{60} at room temperature, despite the presence of fast orientational disorder, that mainly determine the width of the photoemission peak without the need of invoking vibrational broadening.

On the other hand, there is the indisputable evidence of important vibrational contributions to the gas-phase photoemission spectra and there is a strong similarity between the HOMO line shape of these spectra and the spectra of 2D-C_{60} islands on graphite. Moreover, Brühwiler *et al.*[7] suggest that in 3D C_{60} solid the top most molecular layer contribution to the photoemission spectrum may be shifted with respect to the second molecular layer (and bulk) contribution because of different screening effects, which could explain the width and line shape of the HOMO and HOMO-1 peaks.

Angle resolved photoemission data on A_6C_{60} ($A=K, Rb, Cs$) compounds might help to shine some light on the electronic spectra of C_{60}. Several studies indicate that at saturation doping (6 electrons/molecule) the Rb, Cs, and K fullerides form band insulators.[11–13] The crystal structure is bcc, the LUMO-derived bands are completely filled and there is no room for molecular motions. A_6C_{60} is therefore a very lucky case in which merohedral disorder and electron-electron interactions do not play a role in the photoemission spectra.

II. EXPERIMENTAL

Here we report on the angle resolved and temperature dependent photoemission spectra of K_6C_{60}. An ordered
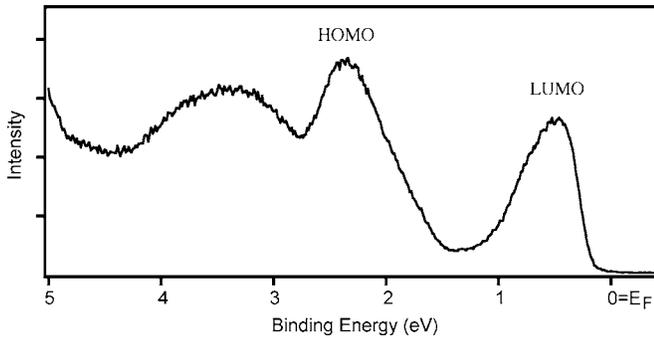
FIG. 1. K_6C_{60} photoemission spectrum collected at 40 K at ISA.

$K_6C_{60}(110)$ thick film was grown on Ag(100) in the ultrahigh-vacuum experimental chamber of the SGM-3 beamline at ISA synchrotron facility in Aarhus (Denmark)[14] where the band dispersion measurements were performed.

In order to reduce the phonon effects as much as possible, measurements of the K_6C_{60} band dispersion were performed at 40 K. The used photon energy was 25 eV, with energy and angular resolution of 25 meV and 0.5°, respectively. Angular scans were performed by moving the analyzer (step 0.25°) with the sample position fixed at 45° from normal incidence. At the photon energy we used, considering an inelastic mean free path of 8 Å for the photoelectrons,[15] the integration in $K_\perp$ is about 25% of the Γ–N direction.

The film orientation was checked by low energy electron diffraction at low temperature. We do not expect changes at higher temperature since no phase transitions are known for K_6C_{60} up to 630 K.

Temperature dependent spectra were measured on the same sample under the same experimental conditions and also on a sample grown in the UHV chamber of the SuperESCA beamline at ELETTRA (Trieste, Italy)[16] using a photon energy of 120 eV. In this latter case the photoelectron were collected by a 150 mm double-pass hemispherical analyzer with an overall energy resolution of 50 meV and an angular acceptance of ±1°.

III. RESULTS AND DISCUSSION

A. Band dispersion

In Fig. 1 is reported a typical photoemission spectrum of K_6C_{60} measured at normal emission. The 0 eV binding energy corresponds to the position of the Fermi level as measured on the clean Ag(100). Here, the nomenclature of the two main features visible in the spectra, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), refers to the orbitals of the undoped C_{60} molecule. Obviously, in K_6C_{60} the HOMO- and LUMO-derived bands are both fully occupied and below the Fermi level (band insulator).

Looking at the available band calculations for K_6C_{60},[17,18] we note that both LUMO-derived and HOMO-derived bands are quite grouped, forming bundles (made of three bands and five bands, respectively) whose energy spread is in some cases small compared to the band dispersion. Under these conditions, there is the possibility to see at least a k dependence of the measured band centroids. However, the coupling with on-ball vibrational modes should be similar to the case of pure C_{60} and, therefore, a similar vibrational broadening and possible polaronic renormalization of the band dispersion should be expected.[7] Wehrli *et al.*[19] have recently pointed out that the broad width of the HOMO- and LUMO-derived bands observed in photoemission experiments on K_6C_{60} has a substantial contribution from the strong coupling with K^+ optic modes, which is not screened in insulating compounds, and that the ground state of a hole created by photoemission in these bands should be polaronic.

The angular dependence of the photoemission spectra along two symmetry directions of the bcc(110) surface, $\bar{\Gamma}-\bar{N}$ and $\bar{\Gamma}-\bar{H}-\bar{N}$, are reported in Figs. 2 and 3, respectively. In both cases there is a clear dispersion of the LUMO-derived and HOMO-derived bands and the dispersion is different for the two symmetry directions. The LUMO dispersion is about 0.3 eV while the HOMO bands show a larger dispersion (the total bandwidth is between 0.6 eV and 1 eV depending on the direction). These numbers are comparable to the estimation based on one-electron band calculations, in particular if we consider that the calculations are made for bulk bands while the photoemission spectra should have a sizable surface contribution, for which a slightly reduced dispersion should be expected because of the reduced coordination number of the C_{60} molecules. In spite of the fact that $K_\perp$ is actually undetermined, by comparing the calculated bulk dispersion along the Γ–N with our measurements, we note that our choice of the photon energy for this bcc(110) surface is particularly fortunate since it appears that $\bar{\Gamma} \sim \Gamma$ and $\bar{N} \sim$ N. Moreover, along the $\bar{\Gamma}-\bar{N}$ we can recognize the presence of at least two HOMO bands, one weakly dispersing and another one dispersing by about 1 eV, which has a good correspondence to the calculated bands.[17] These data indicate that in K_6C_{60} at low temperature (40 K) there is no evidence of strong polaronic renormalization of the bandwidth in the photoemission spectra: The measured angle-resolved photoemission spectra reflect the K_6C_{60} electronic structure and show a reasonable agreement with the one-electron band calculation results.

How does our data compare with undoped C_{60}? The LUMO dispersion measured with inverse photoemission in undoped C_{60} is less than 0.1 eV,[20] while what we measured here on K_6C_{60} is of the order of 0.3 eV. The small dispersion in the inverse photoemission data of C_{60} has been explained primarily with orientational disorder of the molecules (not present in our case) and with the unavoidable Brillouin-zone integration normal to the surface (comparable to our case).[21] The same reasoning can be applied to the HOMO dispersion. Using photon energies similar to the one used here, the measured HOMO dispersion on undoped C_{60} is less than 0.1 eV,[8,9] while on K_6C_{60} we observed a total bandwidth of the dispersion from a group of dispersing bands of $\sim 0.6-1$ eV. Since we do not expect differences in the final-state screening (both compounds are insulators and the photoelectron final state is practically the same) or in the coupling with phonons (the K_6C_{60} case is probably worse because of the further presence of the K^+ modes), once again
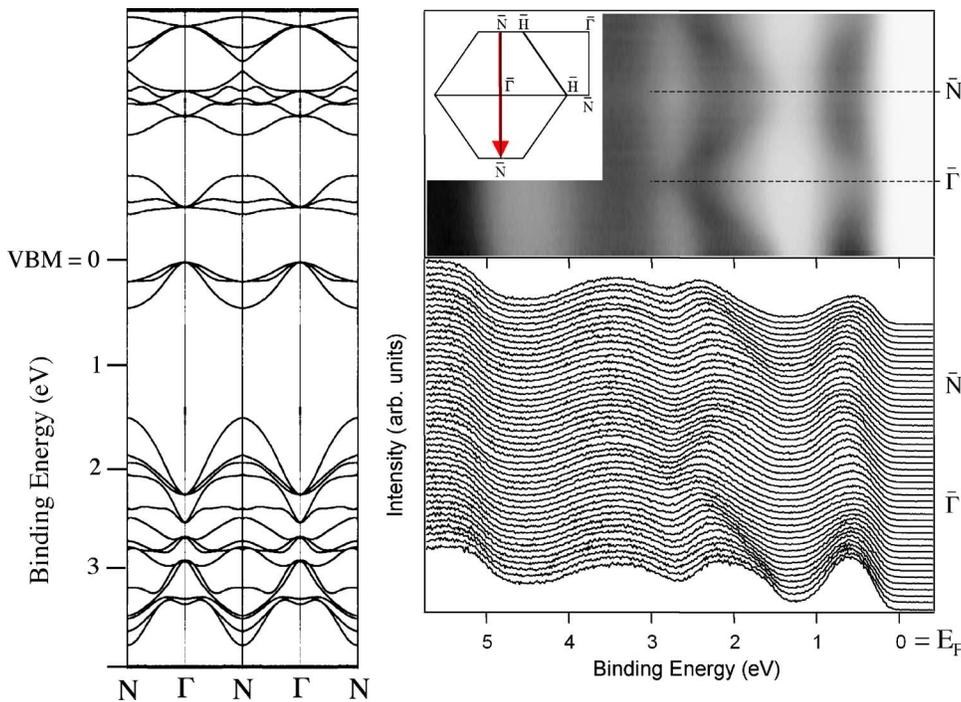
FIG. 2. (Color online) Calculated bulk band structure repeated along the Γ–N direction (left panel) (Ref. 17) and measured band dispersion along the $\bar{\Gamma}$–$\bar{N}$ direction (right panels). The scanning direction on the surface Brillouin zone is shown as inset of the intensity plot panel (white=min, black=max).

the primary difference is the orientational disorder.

The coupling to phonons is, however, evident in our photoemission spectra of K_6C_{60}. Looking at the calculations, we can see that at $\Gamma \sim \bar{\Gamma}$ the bandwidth due to the presence of the three LUMO bands should be very sharp and, even considering our integration in $K_{\perp}$, in the worst case we must expect a width of the photoemission feature of 0.25 eV. The LUMO width observed in the photoemission spectra is at least a factor 2 larger than this expectation, which should be imputed to phonon broadening and in particular, according to Wehrli *et al.*,[19] to the coupling with K^+ modes and the formation of polarons.

The above observations (polaron formation and reasonable band dispersion) may be considered in conflict, but they can be reconciled by a recent work of Rösch and Gunnassonn.[22] Using an adiabatic approximation, Rösch and Gunnassonn have developed a method for calculating the photoemission spectra from systems with strong electron-phonon interactions. This method is particularly simple for systems where the electron-phonon coupling can be neglected in the initial state, e.g., the case of K_6C_{60}. According to the authors, their calculations naturally explain why the electron-phonon coupling leads to a broadening of spectra calculated by neglecting electron-phonon coupling, with minor influence on the dispersion. This can be observed in our angle resolved photoemission data, thus supporting the interpretation that the band dispersion is consistent with one-electron band calculations while the electron-phonon interaction influences the width of the photoemission features.
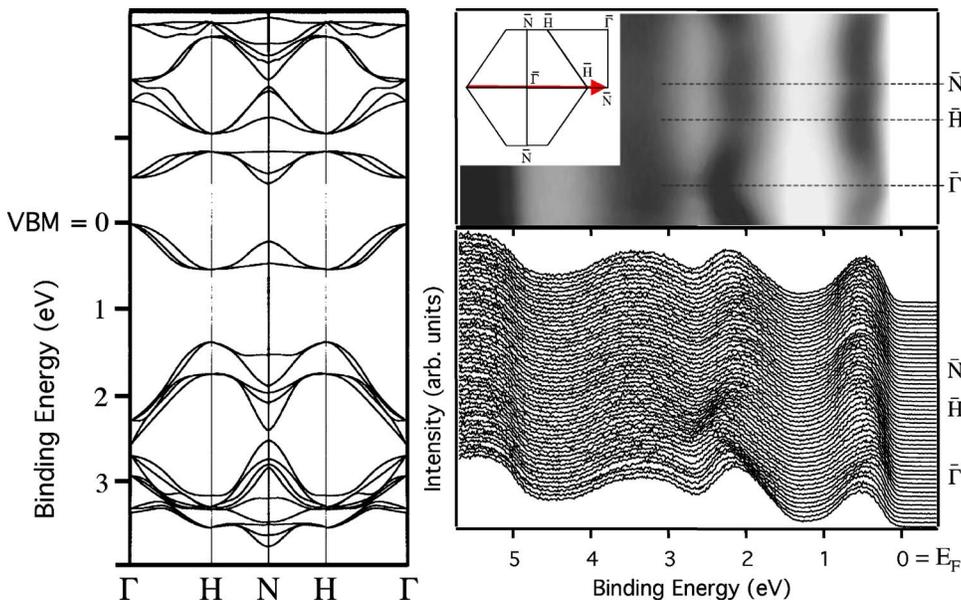

FIG. 3. (Color online) Calculated bulk band structure (Ref. 17) repeated along the Γ–H–N direction (left panel) and measured band dispersion along the $\bar{\Gamma}$–$\bar{H}$–$\bar{N}$ direction (right panels). The scanning direction on the surface Brillouin zone is shown as inset of the intensity plot panel (white=min, black=max).
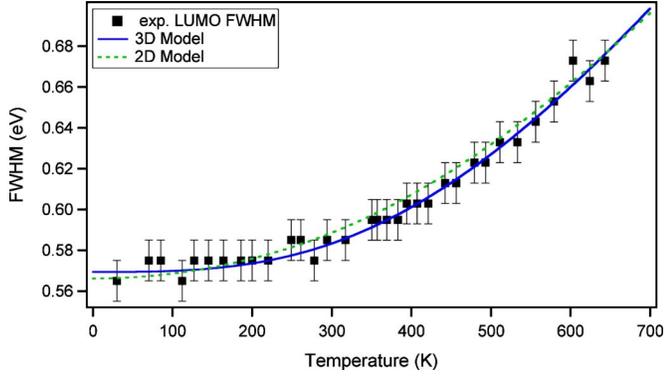
FIG. 4. (Color online) Temperature dependence LUMO line-width in the photoemission spectra as obtained on the raw data (see text for details). Superimposed to the experimental data are the simulations of the observed temperature dependence using Eq. (1) and a two-dimensional (2D, dashed line) or three-dimensional (3D, continuous line) Debye model for the phonon density of states.

B. Temperature dependence

To elucidate the role of phonons in the linewidth of the HOMO and LUMO derived photoemission features we have measured their temperature dependence. Since the binding energy of the electronic states considered is much higher than any phonon energy in K_6C_{60} (i.e., the HOMO and LUMO states are not within a typical phonon energy from the Fermi level) the temperature dependence of the linewidth $W(T)$ is a finger print of the electron-phonon interaction and it roughly follows the temperature dependence of the number of phonons. For the HOMO and LUMO peaks of K_6C_{60}, this phonon contribution to the linewidth can be written as an integral over the phonon energies[23]

$$W(T) = W_0 + W_{e\text{-}ph}(T)$$
$$= W_0 + 2\pi\hbar\int_0^{\omega_D}\alpha^2F(\omega)[1 + 2n(\omega,T)]d\omega, \quad (1)$$

where ω_D is the Debye frequency, $n(\omega,T)$ is the Bose-Einstein distribution, and $\alpha^2F(\omega)$ is the Eliashberg function (which describes the phonon density of states weighted by the electron-phonon coupling parameters). W_0 is a temperature independent contribution to the width typically associated to defects and disorder.

Figure 4 reports the temperature dependent full width at half-maximum (FWHM) of the LUMO feature, as measured on the raw data and corrected by our temperature independent experimental resolution. Fitting the data of Fig. 4 to Eq. (1) requires the knowledge of the Eliashberg function or an approximation of it. As a crude approximation we assume a simple Debye model and the electron-phonon parameter to be a constant λ, so $\alpha^2F(\omega)$ is proportional to the phonon density of states. Since we expect a huge contribution from the surface layer we tried to fit the data by assuming both a two-dimensional and a three-dimensional phonon density of states, i.e., $\alpha^2F(\omega)=[\lambda\omega/\sqrt{(\omega_D^2-\omega^2)}]/\pi$ (2D model) or $\alpha^2F(\omega)=\lambda(\omega/\omega_D)^2$ (3D model).[23] The results of this fitting procedure, by taking $\omega_D=200$ meV (i.e., the highest C_{60}

phonon energy), is reported in Fig. 4 superimposed to the experimental data. Both models provide a good fit of the experimental data (the 3D model being slightly better) with practically the same values for the electron-phonon parameter λ. We obtained $\lambda=1.15\pm0.05$ and $W_0=0.11\pm0.04$ eV. A similar λ value is obtained by considering the temperature dependence of the HOMO width (not shown). If we trust this number, it places K_6C_{60} in an intermediate polaron regime, for which recent quantum Monte Carlo calculations[24] predict a dispersion of the incoherent spectral function (that dominates the spectrum) only slightly reduced with respect to the weak-coupling regime (where the spectrum is dominated by the coherent part and bear a close resemblance with the free-electron case), but with a much more broadened line shape reflecting the stronger coupling to the phonon distribution.

It is worth noting that we have also tried to fit the data of Fig. 4 by using an Einstein model for the Eliashberg function, but the data cannot be fitted satisfactory for any choice of the Einstein frequency.

Although the value of the electron-phonon parameter λ seems consistent with the polaron scenario, the evidence of the strong coupling to the alkali phonons[19] for K_6C_{60} appears contradictory. The experimental data reported in Fig. 4, in fact, seems to show a small contribution to the width from the K^+ vibrational modes, since the width only increases substantially for temperatures larger than the alkali frequencies (i.e., only when the on-ball C_{60} modes are excited). In this respect, however, we have to keep in mind the complexity of the problem and the crudeness of the approximations made above. First of all, it is not necessarily clear that the conditions for the application of Eq. (1) are fulfilled, because the model is only strictly valid for two-dimensional materials.[25] Second, a reliable determination of λ can only be performed if the Eliashberg function of K_6C_{60} is available from theory,[23] other information about the vibrations are available,[26] or if the data could be taken at higher temperature,[25] where the details of the phonon spectrum are irrelevant (this condition is, anyway, impossible since at temperatures higher than 630 K the compound irreversibly transforms into K_4C_{60}).

Despite of these potential problems, the data in Fig. 4 and the corresponding fit provide important qualitative information about the electron-phonon coupling in K_6C_{60}. As already noted above, the coupling to on-ball C_{60} modes must play a major role because of the temperature scale at which we start to see substantial changes in the linewidth, which is larger than the energies associated to K^+ phonon modes. In addition to this, several molecular vibrations are important because otherwise the data of Fig. 4 could be fitted with an Einstein model for the phonon spectrum.

IV. CONCLUSIONS

Low temperature angle-resolved photoemission spectra of $K_6C_{60}(110)$ films demonstrate that the HOMO and LUMO features, although having a linewidth larger than the one-electron band dispersion, show momentum dispersion comparable to band calculations at variance, apparently, to the case of undoped C_{60}. However, this is in agreement with the

predictions of recent calculations for an intermediate polaronic regime of the photo-hole ground state, as suggested by a crude estimation of the electron-phonon coupling constant λ obtained from the temperature dependence of the HOMO-derived and LUMO-derived photoemission feature linewidths. The role of the coupling to alkali phonons in determining the linewidth of the photoemission features remains contradictory: while calculations suggest an important contribution from K^+ phonons, our experimental data seem to suggest that the main contribution comes from intramolecular C_{60} modes. All considered, our data, when compared to undoped C_{60}, point to the importance of the orientational disorder in drowning the band dispersion in the undoped C_{60} spectra.

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