Temperature-Dependent Fermi Gap Opening in the $c(6 \times 4)$–C_{60}/Ag(100) Two-Dimensional Superstructure

C. Cepek,[1] I. Vobornik,[1] A. Goldoni,[2] E. Magnano,[1] G. Selvaggi,[3] J. Kröger,[4] G. Panaccione,[1]
G. Rossi,[1,3] and M. Sancrotti[1,5]

[1]*Laboratorio Nazionale TASC-INFM, Strada Statale 14, km 163.5 Basovizza, I-34012 Trieste, Italy*
[2]*Sincrotrone Trieste S.C.p.A, Strada Statale 14, km 163.5 Basovizza, I-34012 Trieste, Italy*
[3]*INFM and Dipartimento di Fisica, Universita' di Modena e Reggio Emilia, Via Campi 213/A, I-41100 Modena, Italy*
[4]*Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland*
[5]*INFM and Dipartimento di Matematica e Fisica, Universita' Cattolica del Sacro Cuore, Via dei Musei 41, I-25121 Brescia, Italy*

(Received 2 October 2000)

High-resolution angle-integrated photoemission of one monolayer of C_{60} chemisorbed on Ag(100) shows the reversible opening of a gap at the Fermi level at temperatures $25 \leq T \leq 300$ K. The gap reaches a maximum value of ≈10 meV at $T \leq 70$ K. This finding is the first evidence of an electronic phase transition in C_{60} monolayers and has implications on the ongoing debate about surface superconductivity in C_{60}-based bulk materials.

DOI: 10.1103/PhysRevLett.86.3100 PACS numbers: 71.20.Tx, 73.21.–b, 74.25.–q, 79.60.Dp

The discovery of fullerides, and, in particular, of superconductivity in some alkali or rare earth doped bulk C_{60} systems [1], initiated one of the notably active research fields in solid state physics [2]. Recently, major attention was dedicated to the characterization of low-dimensional C_{60} films [3,4]. This is based on an important finding that the superconductivity persists in the surface (mono)layer with a T_c as high as the one in three-dimensional bulk systems. Furthermore, the possibility of controlling at a fine scale the charge state of single C_{60} molecules and the buckyball-buckyball distance makes the fullerene-based films extremely charming for a wide range of applications. The very recent example is the field effect induced charge transfer in a topmost layer of C_{60}, giving a basis for an insulator-to-superconductor switch operating at 11 K [3]. In addition, chemical and physical properties of low-dimensional C_{60}-based layers [5] may be considered superior to the bulk materials, prepared by means of standard intercalation methods and plagued by the presence of multiphases.

Until now, a number of fascinating properties of low-dimensional ordered C_{60}-based films have been reported [6]; however, fewer studies investigated the behavior of the electronic structure and molecular arrangement as a function of T.

We report here a high-resolution photoemission investigation of the electronic properties of one monolayer (ML) C_{60} grown on top of the Ag(100) surface. We observe the opening of an energy gap at the Fermi level when the temperature is lowered from 260 to 25 K. The gap opens and closes reversibly. In the lack of the theoretical knowledge, we discuss possible different origins for this temperature-dependent phase transition in the electronic structure of a two-dimensional C_{60} film.

The experiments were performed in ultrahigh vacuum at a base pressure of $\sim 1 \times 10^{-10}$ mbar. The clean and well ordered Ag(100) surface was obtained by standard procedures [7]. The surface quality was checked via photoemission, Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). Pure C_{60} (99.9%) was sublimated at ~750 K from a Ta crucible. The overlayer coverage was monitored by AES and photoemission spectroscopy. These were calibrated against the coverage of one monolayer of C_{60} that can easily be obtained by depositing a multilayer at room temperature and annealing at $T \geq 500$ K for several minutes [7]. The measurements reported here correspond to a well ordered single layer obtained by depositing C_{60} molecules on the clean Ag substrate maintained at ≈700 K. During the deposition, the pressure remained in the 10^{-10} mbar range.

High-resolution photoemission from the valence band was performed at the low-energy experimental station of the APE beam line, currently under construction at ELETTRA (Trieste). This system is equipped with a Scienta SES-2002 electron energy analyzer and a high-stability He discharge lamp ($h\nu = 21.2$ eV). The overall instrumental energy resolution is better than 10 meV, while the angular resolution is ≈ ±0.4°. Unless differently specified, all reported valence band spectra were acquired in normal emission and normalized to the photon flux. We point out that, because of the small Brillouin zone (≈6°) and the scattering effects due to a large number of C atoms per molecule, the reported photoemission spectra represent electrons scattered over all k vectors within the first Brillouin zone.

The ordered C_{60} monolayer formed on the Ag(100) substrate is characterized by a sharp LEED pattern revealing a c-(6×4) quasihexagonal superstructure [8]. The C_{60}-C_{60} distance in the overlayer is ≈10.42 Å. Keeping in mind that the T_c in C_{60}-based superconducting materials scales with the buckyball-buckyball distance [9], this number should be compared with 10.03 Å in the nonsuperconducting face-centered-cubic C_{60} and, in particular, with 10.43 Å in the highest-T_c Cs_3C_{60} [10]. Recent scanning

0031-9007/01/86(14)/3100(4)$15.00

tunneling microscopy data demonstrate the superstructure remains stable over a wide temperature range [11].

A series of photoemission spectra from the 1-ML C_{60}/Ag(100) is given in Figs. 1(a) and 1(b) as a function of temperature. All spectra are referenced to the Fermi level (E_F), which was determined from the spectra measured on a polycrystalline Ag sample at four different temperatures over the spanned temperature range, and then fitted by the Fermi-Dirac distribution function. The E_F position remained stable (within ± 1 meV) during the measurement time. By each spectrum of Figs. 1(a) and 1(b), we also show the Fermi-Dirac distribution function at a given temperature, referenced to the measured E_F. The spectra from the 1-ML C_{60}/Ag(100) superstructure are characterized by a broad peak near E_F, which represents a portion of the lowest unoccupied molecular orbital (LUMO). This orbital is partially filled by the electronic charge transferred from the metallic substrate to the C_{60} cages. As found previously, the LUMO-related emission at 300 K exhibits a clear Fermi edge, thus indicating a metallic state of the 1-ML C_{60} ordered layer [8].

We notice that the emission close to E_F cannot be due to the substrate since the C-related features are definitely favored in terms of the relative photoionization cross sections at $h\nu = 21.2$ eV ($\sigma_{\mathrm{Ag}5s}/\sigma_{\mathrm{C}2p} \approx 0.03/6$) [12]. We also point out that the escape depth associated with the photoelectrons of Figs. 1(a) and 1(b) favors the adlayer-related contribution with respect to the substrate. In fact, at $\approx$16–17 eV kinetic energy, the electron escape depth in C_{60} is less than the molecular diameter, so the photoemission signal comes exclusively from the C_{60} overlayer [4]. In comparison, the pure solid C_{60} behaves as a semiconductor with a clear zero intensity in the photoemission spectra spanning the whole energy range between the highest occupied molecular orbital and the Fermi level.

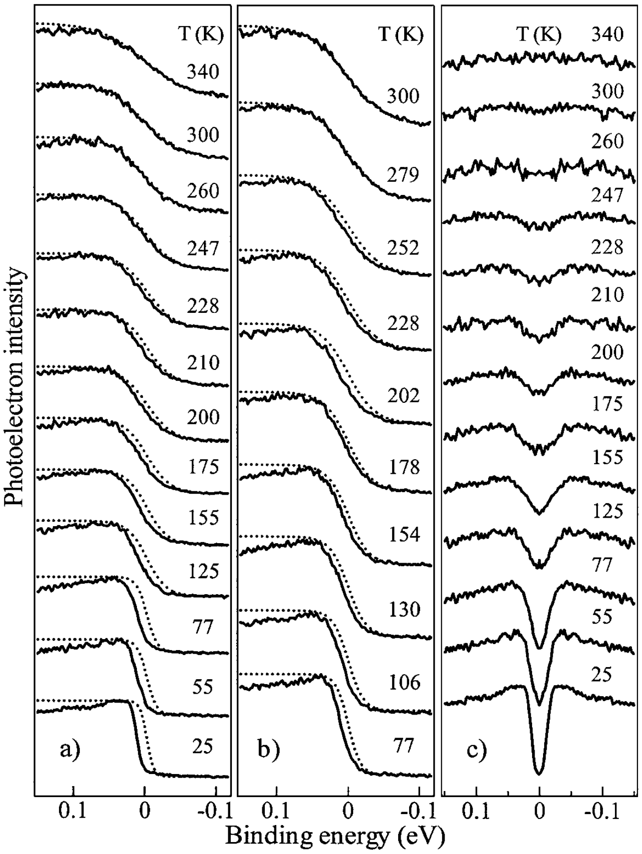

FIG. 1. Valence band photoemission spectra of the LUMO-related spectral feature of the 1-ML C_{60}/Ag(100) system taken as a function of (a) increasing temperature; (b) decreasing temperature. (c) Symmetrized spectra from (a) illustrating the opening of a gap at E_F. All spectra are normalized to the maximum intensity.

The most remarkable effect shown in Figs. 1(a) and 1(b) is the evolution of the spectral intensity in the near E_F region with temperature. From $\approx$260 K downward, a progressive depletion of the photoemission intensity close to E_F occurs. At the same time, the spectral weight accumulates at higher binding energy, giving rise to an unambiguous energy gap opening at E_F. This is emphasized in Fig. 1(c), where the symmetrized spectra with respect to the Fermi level are shown, following the practice developed for analysis of the gap evolution in high-T_c cuprates [13].

Again inheriting the procedure from high-T_c superconductors, we determine Δ as a shift of the spectral leading edge from E_F [14]. We recall that this procedure gives only a qualitative measure of the gap, while the real gap should be determined by fitting the spectra with a known density of states (DOS). Figure 2 illustrates Δ vs temperature. It increases/decreases monotonously, reaching a value of $\approx$10 meV at $T \leq 70$ K. This is independent of the way the temperature is varied.

For a more detailed analysis of the intensity evolution, we consider the difference curves between the spectra at 300 K and the spectra at $T < 300$ K. Figure 3(a) illustrates this analysis for the 25 K spectrum. The difference

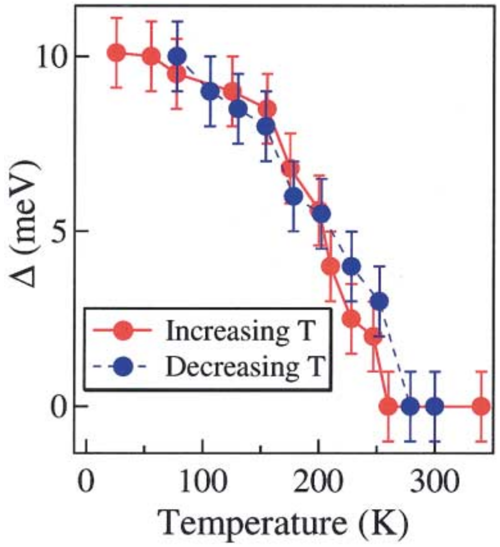

FIG. 2 (color). Plot of the gap (measured as a shift of the spectral leading edge from E_F) vs temperature.

curve exhibits a positive peak centered at ≈30 meV binding energy, and a negative peak centered at $\approx E_F$. We calculated the intensities of the positive and the negative features. The result of this analysis is shown in the inset. As seen from the figure, the positive and the negative features compensate for all temperatures, indicating that the spectral intensity remains constant in the energy interval of ≈250 meV and the spectral weight simply shifts between different binding energies. This also means that the temperature-dependent gap opening occurs at a constant value of the average charge state of the C_{60} molecules. Finally, in Fig. 3(b) we present the spectra taken on the 1-ML C_{60}/Ag(110) at 100 and 300 K. In contrast to the 1-ML C_{60}/Ag(001), we did not observe any gap opening within the explored temperature range.

The mechanism(s) governing the gap opening observed in Fig. 1 is(are) presently unknown. Different scenarios can be speculatively proposed to explain this effect. The extensive studies of 1-ML C_{60}/Ag(100) were focused in the past onto its electronic structure, molecular arrangement, and vibrational properties [8,11,15]. It was found that a combination of the so-called interfacial dynamical charge transfer (IDCT) [16] and Jahn-Teller (JT) molecular distortions may give rise to a charge density wave distributed over the C_{60} molecular pattern.

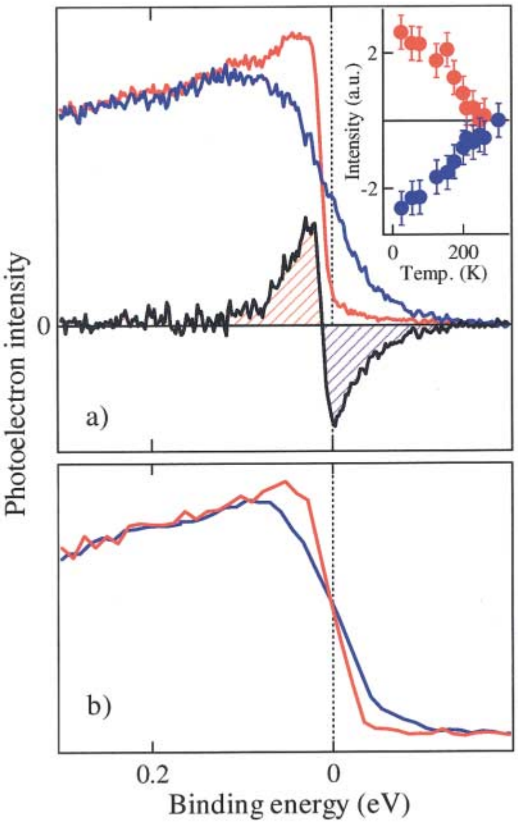

FIG. 3 (color). (a) The spectra from Fig. 1(a) at 300 K (blue) and 25 K (red), together with their difference (dashed) illustrating the evolution of the spectral line shape near E_F with temperature. Inset: Integrated intensity of the positive (red) and negative (blue) features of the difference curves vs T. (b) The spectra from the 1-ML C_{60}/Ag(110) at 300 K (blue) and 100 K (red): no gap opens within the explored temperature range.

In fact, because of their charge state (≈2 electrons/molecule are transferred from the substrate), the C_{60} molecules in 1-ML C_{60}/Ag(100) are expected to undergo cooperative dynamic JT distortions. Since only the symmetric JT-active $A_g(1,2)$ modes are allowed to drive the IDCT, this mechanism is strictly related to the JT distortions of the C_{60} molecules. It was suggested that the JT distortion of C_{60} in the proximity of the Ag(100) surface is strongly anharmonic [8]. This anharmonicity eventually results in a transition from a dynamical to a static distortion regime as a function of decreasing temperature [17]. In other words, lowering the temperature freezes the molecular distortion and, in turn, a change in the DOS with respect to the average value at 300 K is observed. In this case, the balance between on-ball electron-electron interactions and the metallic screening becomes crucial for a stabilization of the charge density wave (CDW) state [18]. The CDW DOS is characterized by a dip at E_F due to the opening of an energy gap, and by a sharp peak a few tens of meV below E_F [18], in agreement with the data of Figs. 1 and 3. This scenario might also explain why the same behavior is not observed in the C_{60}/Ag(110) overlayer, where the correlation effects are expected to be weaker due to the shorter C_{60}-C_{60} distance (≈10.03 Å) [Fig. 3(b)].

The line shape analysis of the fine structure of the LUMO-related photoemission spectra allowed us to measure the electron-phonon (e-ph) coupling in 1-ML C_{60}/Ag(100) [8]. A total e-ph coupling constant (≈1.14) and the role of relevant multiphonon replicas suggest that this system belongs to the intermediate to strong e-ph coupling limit.

A long-standing issue for C_{60}-based systems is whether the prominent e-ph coupling can give rise to the superconductivity even in the presence of strong electronic correlations [2]. Already in the early 1990s, it was recognized that the Coulomb repulsion energy U in doped C_{60} is significantly larger than the electronic bandwidth W [2]. This would render A_3C_{60} a Mott-Hubbard insulator instead of a metal, as experimentally observed. The persisting metallicity was first tentatively explained by a nonstoichiometry of the real sample [19], similar to the case of high-T_c superconductors. The most recent interpretation is based on the threefold degeneracy of the LUMO band [2].

It is important to realize that the energy scale related to the gap opening (∼250 K ≡ ≈21 meV) is significantly smaller than the total energy range over which the spectral weight transfer occurs (≈250 meV; see Fig. 3). Similar behavior is found at the Mott-Hubbard transition in Ni and Mn perovskite oxides [20,21], and it is related to a possible competition between different correlation mechanisms present in the strong U limit. It cannot be excluded that a similar competition drives the gap opening at ≈250 K in the 1-ML C_{60}/Ag(100) system.

A lack of the transport data does not allow deciding whether the gap opening corresponds to a transition from the normal to the superconducting state. From Fig. 3(a), it is quite evident that, along with the progressive sharpening of the spectral leading edge, the decreasing temperature induces a highly peaked emission at ≈ 30 meV binding energy. This spectral evolution is similar to the one observed in high-T_c cuprates when going from the normal to the superconducting state [22]. Evidence from photoemission for the superconducting transition in bulk C_{60} fullerides was reported before both K_3C_{60} and Rb_3C_{60} [4,23]. The report by Hesper *et al.* [4], in particular, points out the change in the line shape consistent with the transition to the superconducting state. This line shape evolution corresponds to the one observed in Fig. 3(a).

In the BCS framework, the ratio $2\Delta_{SC}/k_B T_c = 3.528$ would imply an energy gap as large as ≈ 70 meV. Interestingly, the spectra do show an intensity pileup at the binding energy corresponding to one-half of such a gap ($\Delta_{SC} = 35$ meV), as expected for the condensate peak in the superconducting samples. Fitting the spectra with the BCS gap function, convoluted by the experimental resolution, results in smaller Δ_{SC} values (≈ 25 meV). Nevertheless, even if dealing with superconductivity, its likely unconventional nature may require a DOS different from the BCS one.

The critical temperature where the gap opens is at least 100 K higher than any critical superconducting temperature measured thus far (Fig. 2) [24]. However, in the presence of the strong correlation effects, the temperature where the gap opens does not necessarily need to coincide with the superconducting T_c. In fact, the most peculiar behavior in the high-T_c cuprates occurs in the low doping regime, where a normal state gap (pseudogap) is found to persist at temperatures as high as ≈ 250 K [25].

Other features of the 1-ML C_{60}/Ag(100) system seem also to favor the provocative superconducting scenario. As remarked before, the buckyball-buckyball distance in our system is extremely close to the one in Cs_3C_{60}. Recent ultraviolet photoemission spectroscopy data on 1-ML C_{60}/Ag(100) with highly controlled K intercalation allowed the determination of the charge state of the buckyballs as a function of doping [26]. From these measurements, the charge state in pure 1-ML C_{60}/Ag(100) was estimated to be ≈ 2 electrons per molecule. This value is smaller than in the superconducting A_3C_{60}. We recall, however, that in the field effect device the superconducting state [3] was maintained with the valence of the topmost molecules varying between 2.3 and 3.5, which resulted in a very little change in T_c.

In conclusion, high-resolution photoemission data reveal evidence for a temperature-dependent gap opening in the 1-ML C_{60}/Ag(100) system. This result is of particular significance in light of the recently revealed importance of the surface layer to the superconductivity in C_{60}-based systems. The possible explanations for the observed behavior range from the strong correlation effects to superconductivity (with extremely high T_c), or a combination of the two. At this early stage of investigation, different scenarios cannot be excluded either. In order to distinguish between the different mechanisms, either transport data or a correct form of the DOS at low T is crucial. Experimental and theoretical effort, thus far devoted to three-dimensional bulk systems, will need to be extended to low-dimensional structures in order truly to understand the peculiar properties of the C_{60}-based systems.

The authors are deeply indebted to Erio Tosatti, Luciano Pietronero, and Marco Grioni for fruitful discussions. We are grateful to Gilio Sandrin for his technical support. This work was partially financially supported by the INFM within the project CLASS and by the CNR within the project FILINCLUBE. One of us (J. K.) acknowledges financial support by the Swiss National Science Foundation.

[1] R. M. Fleming *et al.,* Nature (London) **352**, 787 (1991).

[2] O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997).

[3] J. H. Schön, Ch. Kloc, R. C. Haddon, and B. Batlogg, Science **288**, 656 (2000).

[4] R. Hesper, L. H. Tjeng, A. Heeres, and G. A. Sawatzky, Phys. Rev. Lett. **85**, 1970 (2000); (private communication).

[5] A. Goldoni, S. L. Friedman, Z.-X. Shen, and F. Parmigiani, Phys. Rev. B **58**, 11 023 (1998).

[6] Y. Kuk *et al.,* Phys. Rev. Lett. **70**, 1948 (1993); S. Modesti, S. Cerasari, and P. Rudolf, Phys. Rev. Lett. **71**, 2469 (1993); A. J. Maxwell *et al.,* Phys. Rev. Lett. **79**, 1567 (1997).

[7] C. Cepek, Ph.D. thesis, Universität Zürich, 2000.

[8] A. Goldoni *et al.,* Phys. Rev. B **58**, 2228 (1998).

[9] T. Yildrim *et al.,* Solid State Commun. **93**, 269 (1995).

[10] M.-Z. Huang, Y.-N. Xu, and W. Y. Ching, Phys. Rev. B **46**, 6572 (1992).

[11] C. Cepek, L. Giovanelli, M. Sancrotti, G. Costantini, C. Boragno, and U. Valbusa, Surf. Sci. **454–456**, 766 (2000).

[12] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[13] M. R. Norman *et al.,* Nature (London) **392**, 157 (1998).

[14] J. M. Harris *et al.,* Phys. Rev. Lett. **79**, 143 (1997).

[15] C. Cepek, R. Fasel, M. Sancrotti, T. Greber, and J. Osterwalder, Phys. Rev. B **63**, 125 406 (2001).

[16] A. Peremans *et al.,* Phys. Rev. Lett. **78**, 2999 (1997).

[17] K. H. Johnson, M. E. McHenry, and D. P. Clougherty, Physica (Amsterdam) **183C**, 319 (1991).

[18] S. K. Sarker, Phys. Rev. B **49**, 12 047 (1994).

[19] R. W. Lof *et al.,* Phys. Rev. Lett. **68**, 3924 (1992).

[20] I. Vobornik *et al.,* Phys. Rev. B **60**, R8426 (1999).

[21] A. Chainani *et al.,* Phys. Rev. B **56**, R15 513 (1997).

[22] J. M. Imer *et al.,* Phys. Rev. Lett. **62**, 336 (1989).

[23] C. Gu *et al.,* Phys. Rev. B **50**, 16 566 (1994).

[24] A. Schilling, M. Cantoni, and H. R. Ott, Nature (London) **363**, 56 (1993).

[25] H. Ding *et al.,* Nature (London) **382**, 51 (1996).

[26] C. Cepek, M. Sancrotti, T. Greber, and J. Osterwalder, Surf. Sci. **454–456**, 467 (2000).