

BCS-like Density of States in Superconducting A_3C_{60} Surfaces

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We report on an ultrahigh resolution photoemission study on the topmost molecular layer of K_3C_{60} and Rb_3C_{60} films below and above the superconducting transition temperature T_C . We observed not only clear evidence for the opening of the superconducting gap, but also a modification in the photoemission line shape consistent with a change from a normal-metallic to a BCS-like density of states, including the formation of a condensation peak. The data can be accurately modeled by a BCS-type function with a gap Δ derived from T_C in the weak-coupling limit ($2\Delta/k_B T_C = 3.53$).

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The superconducting energy gap Δ is one of the many parameters of the superconducting state of A_3C_{60} ($A = K, Rb$) materials that researchers have been trying to establish experimentally (for an extensive review, see Ref. [1]), as it is of prime importance for the successful understanding of the pairing mechanism. If we consider the reduced gap $2\Delta/k_B T_C$, with T_C the superconducting transition temperature, it seems that bulk-sensitive techniques (e.g., nuclear magnetic resonance (NMR) [2–5], muon spin rotation (μ SR) [6], specific heat [7], and optical spectroscopy [8–11]) usually find values in the range of 3–4, which is reasonably consistent with the reduced gap found in BCS theory in the weak-coupling limit (3.53) and with detailed *ab initio* calculations of the electron-phonon coupling constants [12–15]. More surface-sensitive experimental techniques, on the other hand, like tunneling and photoelectron spectroscopy, produce results that differ considerably among each other. Tunneling spectroscopy studies [11,16–19], for example, yield values for the reduced gap ranging from 2 to 5, probably depending on sample preparation and handling. One problem with these tunneling measurements is that none of them were carried out in ultrahigh vacuum (UHV) conditions, so that the actual state of the surface is unknown. Also a high-resolution photoemission study [20], the only one carried out so far that we are aware of, reveals rather inconsistent results, since the observed opening of the superconducting gap is not accompanied by changes in the spectral line shape that are required to conserve the total density of states.

The surface of C_{60} materials is of special interest in itself. Very recently, Schön *et al.* [21] demonstrated that the surface layer (or interface layer with Al_2O_3) of a pristine (i.e., undoped) and insulating C_{60} single crystal can be driven into a superconducting state in a field-effect transistorlike device. It is remarkable that such a two-dimensional superconductor in the interface monolayer of C_{60} exists with a T_C close to that of the three-dimensional A_3C_{60} compounds, in which a coherence length of 30 Å has been determined [1], about 3 times the thickness of a monolayer of C_{60} .

Here we report on ultraviolet photoemission measurements on K_3C_{60} and Rb_3C_{60} films with a resolution high enough to observe the changes in the line shape upon crossing T_C . Making use of the small inelastic mean free path for the photoelectrons, we are essentially detecting the photoemission signal that originates almost exclusively from the topmost molecular layer of the films [22,23]. These films are well-characterized *in situ*, both by their valence-band photoemission spectra as well as by their temperature dependent resistivity [24].

The experiments were performed in a combined photoemission and electrical transport setup, with *in situ* sample preparation facilities and a base pressure better than 5×10^{-11} mbar throughout. Samples were made by evaporating C_{60} from a thoroughly degassed Knudsen cell at a rate of approximately 1 monolayer per minute onto Al_2O_3 substrates kept at a temperature of 200 °C. The thickness of the films was about 200 nm. The films were doped with potassium and rubidium emitted from thoroughly degassed SAES getter sources while the substrates were kept at 200 °C. The doping level was monitored by way of the resistivity, and the dopant flux was turned off immediately upon reaching the resistance minimum, a method shown to give samples with a high density of states at the Fermi level, a low residual resistivity, a positive temperature coefficient, and a high superconducting transition temperature [24], consistent with studies based on single crystals of C_{60} .

The substrates were rectangular, randomly oriented Al_2O_3 single crystal plates, polished to a surface roughness of less than 10 Å. Electrical contacts, consisting of 80 nm Ag on a 20 nm Ti binding layer, were evaporated *ex situ* on the substrates prior to introduction into the vacuum system. The substrates were clamped with stiff molybdenum springs onto a copper sample holder mounted on a Janis Supertran continuous flow cryostat. Temperature was measured with a Si diode mounted on the cryostat and a Pt-1000 resistor directly next to the sample. Because of the required free access for evaporation and spectroscopy purposes, no thermal shielding was employed. Nevertheless, since the measured T_C

of the doped films was always within 1 K from the highest literature values, we are confident that the actual sample temperature never deviated more than 1 K from the measured one. Electrical resistance was measured with a Stanford Research Systems lock-in amplifier and a precision current source at a frequency of a few hertz. The current was $10 \mu\text{A}$, far below the critical current of the films. The spectrometer consisted of a modified VSW 150 mm hemispherical electron energy analyzer fitted with a multichannel detector and an Omicron gas discharge lamp operating at the He-I resonance line ($h\nu = 21.22 \text{ eV}$). Within the small energy window of interest ($\pm 40 \text{ meV}$ binding energy), we found that the He-I satellite (2%) gives only a small and essentially constant background signal that can be subtracted together with the dark current of the detector. Because the samples were polycrystalline, the photoemission spectra were effectively angular integrated.

To determine the energy resolution of the spectrometer, tests were performed on a clean Pt sample at low temperature. Figure 1 shows a spectrum recorded at 9 K. A good fit to the spectrum is obtained using a linear density of states multiplied with a Fermi-Dirac function for a temperature of 9 K, and convoluted with a Gaussian with a full width at half maximum (FWHM) of 7.5 meV and a Lorentzian with a FWHM of 2.2 meV, giving an overall resolution of about 8.7 meV. The Lorentzian contribution improves the fit appreciably, representing probably the lifetime broadening of the He-I spectral line. It turned out that both the lens functions of the electron energy analyzer and the gas pressure in the helium lamp critically influenced the resolution of the measurements. To facilitate reliable comparisons, the C_{60} spectra presented below were taken under exactly the same conditions as the Pt

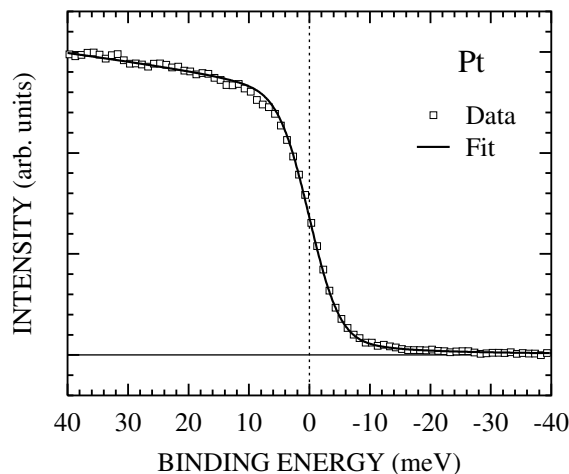


FIG. 1. Photoemission spectrum around the Fermi level of a clean Pt sample at 9 K (squares). The spectrum is fitted (solid line) by a linear density of states multiplied with a Fermi-Dirac function at 9 K, and convoluted with a Gaussian (FWHM = 7.5 meV) and a Lorentzian (FWHM = 2.2 meV) to account for the instrumental broadening.

spectrum in Fig. 1. Long-term thermal drift of the order of maximally $\pm 0.5 \text{ mV}$ per hour in the digital-to-analog converters caused an uncertainty in the calibration of the absolute position of the Fermi level of the same magnitude. To eliminate this effect, and obtain an accurate reference for any shifts resulting in the opening of a gap, the high-resolution spectra were taken as several separate short scans, alternatingly below and above T_C , which were afterwards summed up when no significant shifts in the Fermi cutoff were seen.

In Fig. 2, the resistivity of the K_3C_{60} and Rb_3C_{60} films as a function of temperature is shown. The temperature coefficients are positive (“metalliclike”) over almost the entire temperature range and the resistivities just above T_C have low absolute values (0.5 and 0.65 $\text{m}\Omega \text{ cm}$, respectively), indicating good quality of the films. Also the T_C 's (19 and 29 K) are consistent with good samples as reported in the literature [1], although the superconducting transition of Rb_3C_{60} shows a slight shoulder halfway.

The high-resolution photoelectron spectra of K_3C_{60} and Rb_3C_{60} near the Fermi energy E_F are shown in Figs. 3 and 4, respectively, both below T_C ($T = 6 \text{ K}$) and above T_C ($T = 22 \text{ K}$ for K_3C_{60} and $T = 33 \text{ K}$ for Rb_3C_{60}). The

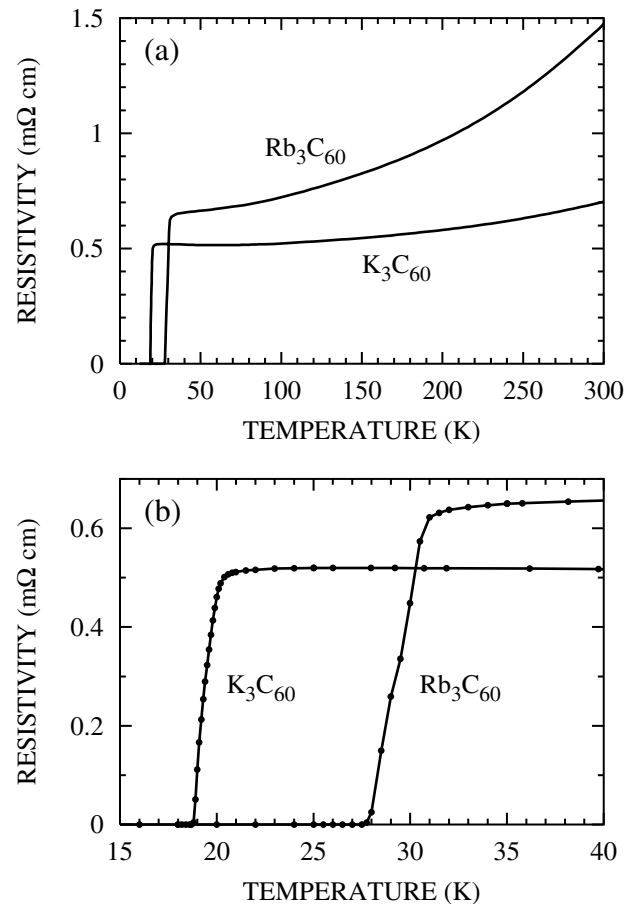


FIG. 2. Temperature dependence of the resistivity of the K_3C_{60} and Rb_3C_{60} films. (a) An overall view up to 300 K, and (b) a close-up near the superconducting transition temperatures.

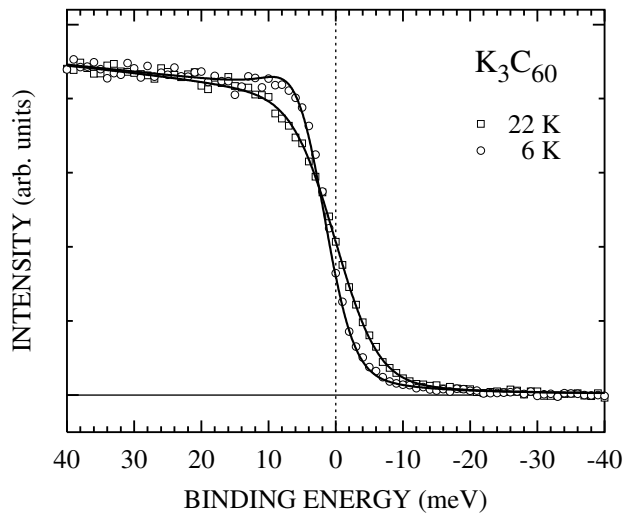


FIG. 3. Photoemission spectra of K_3C_{60} at 22 K (squares) and at 6 K (circles). The data are modeled (solid lines) with, respectively, a Fermi-Dirac function at 22 K and a BCS function with a gap $\Delta = 2.9$ meV, broadened by the resolution functions found for the Pt reference.

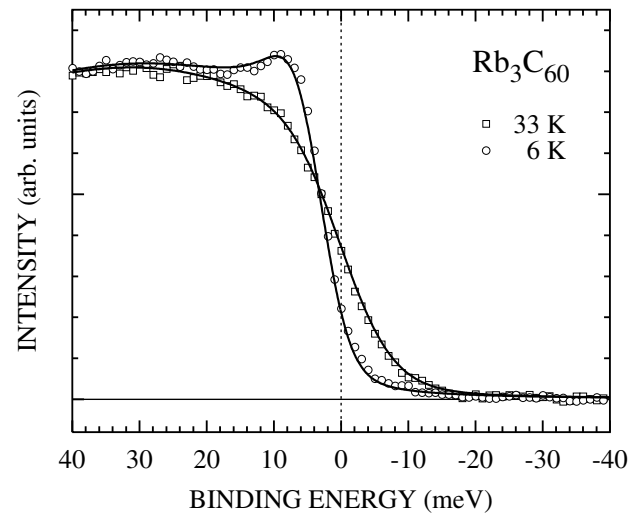


FIG. 4. Photoemission spectra of Rb_3C_{60} at 33 K (squares) and at 6 K (circles). The data are modeled (solid lines) with, respectively, a Fermi-Dirac function at 33 K and a BCS function with a gap $\Delta = 4.4$ meV, broadened by the resolution functions found for the Pt reference.

first thing to notice is that the changes in the spectra are not just a shift in the Fermi level as seen in an earlier photoemission study [20], but that there are actually substantial changes in the line shape. The cutoff becomes sharper in an asymmetrical way, and, especially in the case of Rb_3C_{60} , there is a clear signature of a condensation peak or “pileup” at about 8 meV binding energy, analogous to the Hebel-Schlichter peak seen in NMR and μ SR. Ideally, this peak is expected to occur at exactly the pair-breaking energy, Δ . However, because of the asymmetric shape of the BCS density of states, it shifts as it gets broadened by the instrumental resolution.

To compare the measured data with the expected density of states, the latter is plotted in Figs. 3 and 4 as solid lines through the data points. The normal-state spectra are modeled, as was done in the case of the Pt reference sample, by a Fermi-Dirac function weighed with a slowly varying spectral distribution to account for the structure in the density of states near the Fermi level, and convoluted by Gaussian and Lorentzian broadening functions, which are taken identical (7.5 and 2.2 meV FWHM, respectively) to the ones found for the Pt reference. This provides good fits to the normal-state spectra of both K_3C_{60} and Rb_3C_{60} , confirming that the samples indeed behave in a metallic way, and that the instrumental resolution is consistent.

In the superconducting state the same procedure is followed, except that now a BCS-type density of states $|E|/(E^2 - \Delta^2)^{1/2}$ for $|E| > \Delta$ (and 0 elsewhere) is introduced. The superconducting gap Δ for the plotted curves was derived from the transition temperature using the BCS weak-coupling ratio $2\Delta/k_B T_C = 3.53$, giving $\Delta = 2.9$ meV for K_3C_{60} , and $\Delta = 4.4$ meV for Rb_3C_{60} . As can be seen, these models fit the data rather well, both

in the magnitude of the gap as well as in the position and intensity of the condensation peak.

The quantitative agreement between theory and experiment may actually seem surprising, seen in the light that the photoemission signal in these measurements originates almost exclusively from the topmost molecular layer of the sample, due to the small inelastic mean free path for electrons at the relevant kinetic energy (≈ 17 eV) [22,23]. One would expect the superconducting properties of the surface of a material to be modified by a variety of contributions, such as a different surface composition and a lowered symmetry. Additionally, in the specific case of K_3C_{60} , it was found [24] that the electronic structure of the surface (in the normal state) may differ fundamentally from the electronic structure of the bulk, to avoid the divergence of the electrostatic potential in the crystal associated with its polar (111) surface termination. One has to take into account, however, that the shortest length scale over which the superconducting order parameter can change is the Ginzburg-Landau coherence length ξ , which is of the order of 30 Å in the alkali fullerides [1], rather short for a conventional superconductor, but still considerably longer than the thickness of the top monolayer (≈ 8 Å). It is very likely due to this effect, which is similar to the proximity effect found in superconductor-normal metal interfaces, that the surface layer, irrespective of its own electronic structure, is indistinguishable from the bulk on the scale of the superconducting coherence length.

On the other hand, a more provocative scenario could also be envisioned, in which the surface plays an active role for the superconductivity in A_3C_{60} materials. This is based among others on the very recent achievements by Schön *et al.* [21] mentioned before. They claim that by

means of an electric field about three electrons per C_{60} molecule can be induced in the topmost molecular layer of the C_{60} crystal, with the result that the insulating device becomes conducting and, surprisingly, even superconducting with a T_C as high as 11 K. Most remarkable is that the valence of these C_{60} molecules need not be precisely 3-, as is often claimed to be necessary for bulk cubic fullerides to be superconducting [25]. In the field-effect device, superconductivity can be maintained with the valence of the topmost C_{60} molecules varying between 2.3- and all the way up to probably more than 3.5-, with little change in T_C . This is important, because, as already mentioned above, the surface of K_3C_{60} solids is found to have a completely different electronic structure than the interior of the solid: the valence of the C_{60} ions at the surface is not 3- but 2.5-, and the surface layer is a good metal independent of whether the solid inside is a metal or an insulator [24]. The spectacular results of Schön *et al.* seem to suggest that a metallic surface layer of C_{60} can sustain superconductivity with a high superconducting transition temperature. This, together with the results presented in the current work, brings back into focus the possibility that the grain boundaries in A_3C_{60} (which, like the surface, would also be metallic with a valence of 2.5- rather than 3- [24]) play an important role in the superconducting properties of "bulk" C_{60} compounds.

To conclude, we found with high-resolution ultraviolet photoelectron spectroscopy clear evidence for the opening of the superconducting gap in the topmost molecular layer of K_3C_{60} and Rb_3C_{60} , and we observed changes in the spectral features which are characteristic for a BCS-like superconducting transition. The spectra could be modeled assuming gaps that are consistent with the BCS weak-coupling limit and consistent also with the results of most bulk-sensitive measurements. In view of the recent discovery of electrostatically induced superconductivity in the top monolayer of pure C_{60} , there exists an intriguing possibility that the surface and grain boundaries actually play an active role in the formation of the superconducting phase.

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