Electronic structure and superconducting energy gap in Rb_3C_{60} single crystals studied by photoemission spectroscopy

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We report an ultrahigh-resolution photoemission study of Rb_3C_{60} single crystals ($T_c = 30.5$ K) and the measurement of the superconducting energy gap. The crystals were cleaved at 13 K to expose the (111) plane. They show a sharp Fermi cutoff above T_c and a superconducting gap opening below T_c ($2\Delta/k_BT_c \sim 4.1$ at 13 K). The valence band shows a ~ 0.15-eV-wide band near E_F that is consistent with calculations, and a broad band at 0.15–1.3 eV, possibly contributed by the surface C_{60} layer.

The discovery of superconductivity in the alkali-metal intercalated C_{60} fullerides[1,2] has led to a great amount of effort directed toward understanding the electronic properties and superconductivity mechanism of these novel solids. One of the crucial parameters, the superconducting energy gap, has been probed by tunneling microscopy,[3] optical measurements,[4,5] nuclear magnetic resonance,[6] and muon-spin relaxation experiments.[7] The results, obtained from powdered samples, are quite diverse ($2\Delta/k_BT_c = 3$–5.3), and a consensus on the coupling strength has not been reached. Doping effects in the electronic states have been probed by photoemission spectroscopy (PES) on thin films which were produced *in situ*.[8–16] Most of the studies on K- or Rb-doped A_xC_{60}[8–11,14–16] indicated partial occupation of the t_u lowest unoccupied molecular orbital (LUMO) band for $x \sim 3$ and consequent metallic character of these materials. However, the LUMO-derived band appears to be much broader than that predicted by calculations.[17] It has been interpreted in terms of possible mixing of different crystallographic phases in the samples,[18] or electron-energy losses due to phonon and plasmon couplings.[14,15] Completely different experimental results were reported by Takahashi *et al.*[12,13] showing the existence of a pseudogap structure for K_3C_{60} and Rb_3C_{60}, which was interpreted as supporting the suggestion[19] that stoichiometric K_3C_{60} is a Mott-Hubbard insulator. The significant discrepancies among electron spectroscopy experiments as well as different gap measurements probably result from unknown sample variations. Further studies of fulleride superconductors may require substantially improved sample characterization in terms of the doping level, crystallinity, and superconductivity.

In this paper we report ultrahigh-resolution photoemission studies on stoichiometric, superconducting Rb_3C_{60} single crystals ($T_c = 30.5$ K) cleaved at low temperature, and the observation of the superconducting gap in Rb_3C_{60}. The LUMO-derived valence states at 0–1.3 eV binding energies were observed. The results are compared with calculations and earlier thin-film studies.

The Rb_3C_{60} single crystals were produced by a newly developed one-step doping process.[20] C_{60} crystals and three equivalents of Rb metal were sealed in a quartz tube and annealed extensively at 300 °C. Figure 1 shows a superconducting quantum interference device (SQUID) magnetization measurement for a typical Rb_3C_{60} crystal. It exhibits a sharp superconducting transition at $T_c = 30.5$ K (0.8 K transition width) and approximately 90% superconducting fraction (shielding experiment). Crystals selected for PES measurements were individually measured (SQUID); each showed a T_c transition nearly identical to that in Fig. 1. The (111) orientation can be easily identified by the crystal facets. After the photoemission experiment, x-ray-diffraction measurements were taken on one of the cleaved Rb_3C_{60} crystals, and the fcc (111) orientation of the cleavage plane was confirmed.

Photoemission experiments were conducted at the Wisconsin Synchrotron Radiation Center, using a Seya monochromator as well as a He-I discharge lamp ($h\nu = 21.2$ eV). Photoelectrons were collected by a hemispherical electron-energy analyzer within a $\pm 1°$ solid angle. Samples were mounted on aluminum posts with a

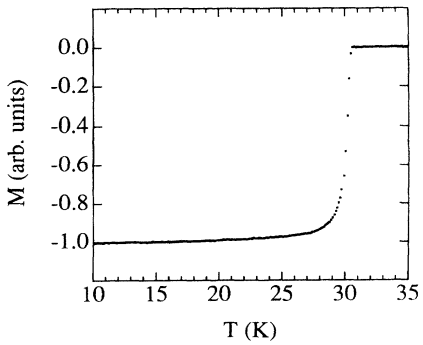

FIG. 1. SQUID magnetization measurement of Rb_3C_{60} single crystals.

vacuum-compatible silver epoxy in an Ar atmosphere. They were transferred into the photoemission chamber through a load-lock system under vacuum. Each crystal was cleaved at low temperature (13 K) in a vacuum better than 5×10^{-11} Torr, and was kept at $T\leq40$ K throughout the experiment. It is well known that Rb may easily diffuse in solid C_{60} at room temperature. Keeping the sample at low temperature may prevent possible Rb interdiffusion near the surface.

Photoemission spectroscopy has recently been successfully used to investigate gap structure on some of the large-gap, high-T_c cuprate superconductors.[21,22] In this study we use PES with significantly improved energy resolution to probe the electron states of Rb_3C_{60} near E_F in the normal and superconducting states. Figure 2 shows the Rb_3C_{60} spectra taken with He-I discharge radiation ($h\nu=21.2$ eV). The data were taken with electron emission at 30° away from the surface normal, where measurement was convenient with the He lamp setup. As discussed later in the paper, Rb_3C_{60} data taken at various angles show little energy dispersion, mainly due to the relatively small Brillouin zone for the crystal. Therefore the data shown in Fig. 2 should be viewed as effectively angle integrated. These data are compared with the Fermi-edge references taken from a cogrounded platinum sheet nearby. Pt reference data were taken before and after measuring Rb_3C_{60} to ensure that no electric drift occurred during data acquisition. The Pt data at both 40 and 13 K were fitted by a linear spectral function convoluted with the Fermi-Dirac distribution and a Gaussian function which represents the instrument broadening. By fitting the Pt Fermi-edge data, we obtained the instrument energy resolution of 13 ± 1 meV and the Fermi level position with a precision of ±0.2 meV. These parameters are used in fitting the Rb_3C_{60} data. At 40 K the leading edge in Rb_3C_{60} matches the Pt Fermi edge very well, indicating normal metallic behavior for Rb_3C_{60}. The 40-K spectrum of Rb_3C_{60} can be well fitted by a linear density of states (DOS) function coupled with the Fermi-Dirac distribution and the instrument broadening obtained from the fit (see the dashed curve). At $T=13$ K, the Pt Fermi edge is sharpened slightly due to reduced thermal broadening, but the edge position does not change. In contrast, the leading edge of the Rb_3C_{60} data at 13 K is pulled to higher binding energy, indicating the presence of a superconducting gap. The Rb_3C_{60} spectrum at 13 K was fitted with the linear DOS function obtained from the fit of the 40-K data multiplied by the divergent BCS-type gap function $E/(E^2-\Delta^2)^{1/2}$. The Gaussian broadening function is convoluted with the model fitting curve. The fit (dashed line) yields a gap $\Delta=5.3$ meV. The reduced gap value, $2\Delta/k_BT_c=4.1$ (for $T=13$ K), is slightly higher than the BCS weak-coupling value of 3.52 for $T=0$ K. Fitting uncertainties, including uncertainty of the E_F position, are estimated to be ±0.5 meV. The data at 13 K appear to be broader than the fit. This might result from unknown thermal broadening and surface layer effects (discussed later in the paper). These effects could also contribute to uncertainty in the gap value.

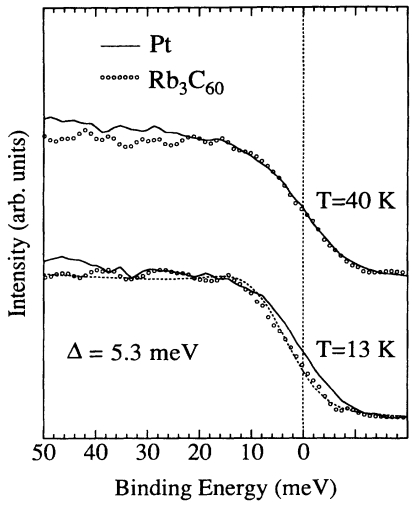

FIG. 2. High-resolution spectra (circles) showing the leading edge of the valence band in Rb_3C_{60} at normal ($T=40$ K) and superconducting ($T=13$ K) states, respectively. The data are compared with the Fermi edge references taken from a cogrounded Pt sheet (solid lines). In the normal state, the Rb_3C_{60} spectrum matches well with the reference Fermi edge, clearly indicating its metallic character. In the superconducting state, the leading edge in Rb_3C_{60} shifts slightly to higher binding energy due to a gap opening. Curve fitting with the BCS-type gap function (dashed line, see text) gives $\Delta=5.3$ meV.

It is important to compare these gap measurements with the tunneling experiments since tunneling also probes changes in the DOS near the Fermi level. Tunneling data obtained by scanning tunneling microscopy show a large reduced gap $2\Delta/k_BT_c=5.3$ in both Rb_3C_{60} and K_3C_{60},[3] indicating a strong-coupling mechanism for these materials. The expected DOS pileup feature was clearly seen in the conductance data at 4.2 K. At higher temperatures (10–15 K) the pileup is significantly broadened and reduced in the conductance data.[3] A pileup feature is not obvious in the present PES data, possibly due to thermal broadening and the relatively large instrument broadening.

Gap values in A_3C_{60} have also been derived by a few other techniques. A smaller gap was found from relative (superconducting to normal state) far infrared reflectivity experiments ($2\Delta/k_BT_c\sim3$–5 for Rb_3C_{60}) (Ref. 4) and from absolute reflectivity measurements ($2\Delta/k_BT_c=3.6$ for K_3C_{60} and 2.98 for Rb_3C_{60}).[5] ^{13}C nuclear-magnetic-resonance[6] (NMR) and muon-spin relaxation[7] experiments indicate a gap scale compatible with the BCS weak-coupling limit. The variation in the obtained gap values may be partly caused by the use of polycrystalline samples in these studies (polycrystalline samples often exhibit large T_c transition widths and low superconducting fractions). More experiments on high-quality crystals are needed before reaching a consensus on the gap energy scale, which is one of the crucial parameters needed in the description of pair coupling.

Another important, but unresolved issue is the experimental valence band structure for the superconducting

fullerides. As mentioned earlier, there has been a continuing debate on the intrinsic electronic states of the superconducting fullerides. Figure 3 shows the PES spectra of the LUMO-derived states measured from a (111) cleaved surface of Rb_3C_{60}. These data were collected with 22-eV photons at $T=13$ K (total resolution ~ 50 meV). Two distinct features can be seen: a narrow band from E_F to ~ 0.15 eV and a much broader band extending from 0.15 to 1.3 eV. Spectra taken at normal emission (corresponding to the electron analyzer setting at $\theta/\phi=0°/0°$) and a few degrees away from the normal show slightly varying intensity for the leading feature near E_F. Normal emission spectra taken with the photon energy tuned from 20.0 to 23.0 eV (not shown) also indicate intensity variation for the narrow band, but energy dispersion is not readily resolved in these data. Detailed observation of energy-band dispersion in Rb_3C_{60} appears to be hindered by the narrow band nature of the molecular solid as well as by the small Brillouin zone of the crystal, relative to the instrumental k-space resolution ($\sim\frac{1}{5}$ of the zone dimension). The 0.15-eV-wide band near E_F, which is also seen in recent studies on improved thin films,[14,15] is consistent with theory and a few other experiments. First-principles calculations on K_3C_{60} (Ref. 17) show partial occupation of the LUMO band. The width of the occupied states is 0.26 eV, but about 80% of the DOS is located within 0.15 eV of the Fermi level. For Rb_3C_{60} the bandwidth should be slightly smaller, relative to K_3C_{60}, because the lattice parameter is larger. Nuclear-magnetic-resonance (NMR) experiments indicated that the DOS at E_F, $N(0)\sim 22$ electrons/eV per C_{60} for Rb_3C_{60}.[23] Normal-state magnetic susceptibility measurements for Rb_3C_{60} have shown $N(0)\sim 19$ electrons/eV per C_{60}.[24] Under the assumption of a uniform DOS in the LUMO-derived conduction band and complete charge transfer from Rb to C_{60}, these $N(0)$ values suggest an occupied band width of 0.14–0.16 eV, in good accord with the current observation of the narrow band near E_F.

The broadening of the LUMO feature at 0.15–1.3 eV is apparently associated with the broadening of the fully occupied highest occupied molecular orbital (HOMO) and HOMO-1 bands at higher binding energies as shown in Fig. 4 (the narrow band near E_F is not well-resolved due to lower resolution of ~ 80 meV for this measurement). The spectrum in Fig. 4 was taken at near-normal emission at 13 K with 22-eV photons. The HOMO and HOMO-1 molecular bands in pristine C_{60} are quite sharp and well separated.[25] However, these bands are significantly broadened in the Rb_3C_{60} data. As illustrated in Fig. 4, the narrow LUMO band near E_F can be associated with a set of low binding energy HOMO and HOMO-1 emissions and the broad LUMO band with a (broadened) duplicate set of features shifted to higher binding energies. Some of the earlier film studies[15] attributed the broadening to nonequilibrium growth of the $x=3$ and $x=4$ (or 6) phases even for overall stoichiometry $x<3$. In the current experiment, however, the Rb_3C_{60} crystals are excellent superconductors dominated by the $x=3$ phase. Therefore the additional set of valence features at higher binding energies is intrinsic to the PES measurements of Rb_3C_{60} (111). We speculate that the shifted spectrum is mostly attributable to the surface layer. The properties of alkali fullerides are very sensitive to intercalation environment. A number of fullerides, including Na_xC_{60}, A_1C_{60}, and A_4C_{60} (A=Rb and K) are not metallic or superconducting,[11,26,27] although the rigid-band-filling scenario may still predict metallic behavior for these compounds. It is possible that the loss of the Rb_3C_{60} intercalation environment on the cleaved surface might induce a nonmetallic C_{60} layer at the surface. The relatively large spectral weight of the set of valence features at higher binding energies in the Rb_3C_{60} data (Fig. 4) is consistent with their assignment to a surface contribution due to the small electron mean free path in C_{60}, which is comparable with the diameter of the C_{60} molecular unit.[28]

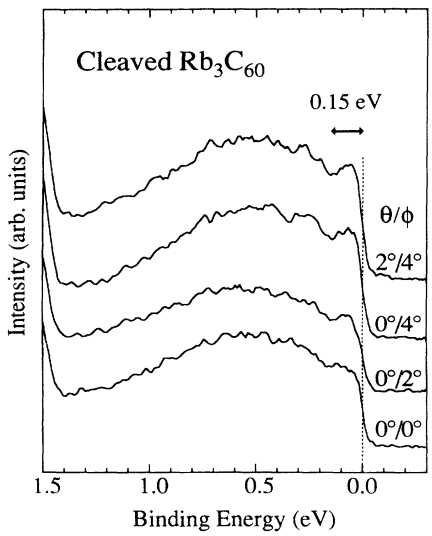

FIG. 3. The LUMO-derived valence band of a Rb_3C_{60} crystal cleaved at the (111) plane at 13 K, showing a ~ 0.15-eV band near E_F and a broad feature at 0.15–1.3 eV.

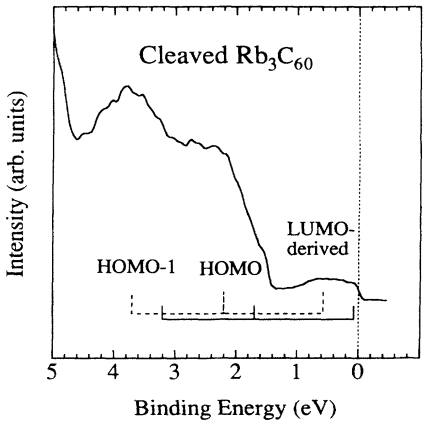

FIG. 4. The valence band of Rb_3C_{60} including LUMO, HOMO, and HOMO-1 levels. The sets of states at lower-binding energies is attributed to bulk Rb_3C_{60}.

Some of the recent thin-film studies have indicated the existence of fine structures in the LUMO band spectra taken at low temperature.[14,15] These structures were considered as possible phonon and plasmon energy loss features. Unfortunately, such fine structures were not clearly seen in Figs. 3 and 4. Due to the high mobility of Rb, the stoichiometry and ordering for thin-film surfaces prepared at $T \geq 300$ K might be different from a surface cleaved at low temperature. In fact, significant temperature-dependent changes in the LUMO spectra were observed for thin films.[14] Apparently, these changes cannot be explained in terms of thermal broadening or excitation. Further comparative experiments on single crystals cleaved at room temperature may be helpful to resolve the issue.

In conclusion, we have conducted high-resolution photoemission experiments on cleaved Rb_3C_{60} single crystals, and measured the superconducting energy gap in Rb_3C_{60}. Rb_3C_{60} shows metallic character in the normal state, and a superconducting gap opening when cooled below T_c. The measured gap is slightly larger than that predicted by the BCS weak-coupling limit. The valence band of Rb_3C_{60} cleaved at the (111) plane shows a ~ 0.15-eV-wide narrow band near E_F, whose appearance is consistent with calculations for bulk Rb_3C_{60}, and an anomalous broad feature at 0.15–1.3 eV, that may be mainly attributed to the surface-vacuum C_{60} termination layer.

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