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Satellites in the photoemission spectra of A_3C_{60} (A = K and Rb)

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The high-resolution photoemission spectral profiles of the conduction bands of K_3C_{60} and Rb_3C_{60} recorded at 10 K exhibit fine structure not observed at higher temperatures. Calculations of the effects of electron-boson coupling in A_3C_{60} within a simple model demonstrate that the features in the low-temperature photoemission spectral weight are consistent with satellites due to phonons and the charge-carrier plasmon. Possible causes of the observed temperature dependence of the conduction-band spectral weight are discussed.

The subject of the detailed electronic structure of A_xC_{60} (A=K and Rb) and particularly the issue of the nature of the electronic states near the Fermi level (E_F) in A_3C_{60}, continues to excite lively debate.[1-5] Despite recent photoemission studies with high resolution and accurate, absolute determination of the doping level,[6,7] the observed width of the occupied conduction band in A_xC_{60} and the low density of states (DOS) at E_F have not been fully understood until now.

In this paper, we report temperature-dependent high-resolution photoemission measurements of the A_3C_{60} system. The shape of the conduction-band-derived spectral weight is seen to change considerably as a function of temperature, with new features apparent in the spectra recorded at 10 K. Calculations of the photoemission spectrum reveal that both the shape and width of the low-temperature conduction-band-derived spectral weight, as well as the DOS at E_F are consistent with the presence of satellites due to both phonons and the charge-carrier plasmon. Possible causes of the observed changes in the conduction-band spectral weight with temperature are discussed.

Polycrystalline A_3C_{60} films of thickness $\sim$100 Å were prepared and characterized as described elsewhere.[6] Photoemission was carried out using He I radiation ($h\nu$=21.22 eV) with an overall energy resolution of 25 meV (angular resolution, $\pm 1°$). The surface doping level was determined from the ratio of the observed conduction-band-derived spectral weight to that of the band derived from the highest occupied molecular orbital (HOMO) of C_{60}. The result was compared with the analogous ratio from a calibration series of photoemission spectra of K_xC_{60} in which *in situ* x-ray photoemission spectroscopy (XPS) studies were conducted together with valence-level photoemission spectra recorded with a wide range of photon energies, including 21.22 eV.[6] The corresponding uncertainty in the absolute x values quoted is ± 0.5.

The calculations of the photoemission spectra were carried out within a simple model in which the Hamiltonian of the system, H, is split into an electronic term, a boson term, and a term describing the electron-boson coupling:

$$H=\varepsilon c^{\dagger}c+\sum_{\nu}\omega_{\nu}b_{\nu}^{\dagger}b_{\nu}+\sum_{\nu}g_{\nu}(b_{\nu}^{\dagger}+b_{\nu})cc^{\dagger}\,. \tag{1}$$

The bosons, of frequency ω_{ν}, describe both the phonons and the plasmon. For the phonons, both the A_g and H_g modes of C_{60} were taken into account. The latter should properly be treated within a more complex Hamiltonian, where a phonon is allowed to scatter an electron between two different conduction-band states, but it is not expected that such an improvement would change the qualitative features of the model. The phonon coupling constants $g_{\rm ph}$ were obtained from *ab initio* calculations.[8] The calculated electron-phonon couplings correspond to the coupling strength $\lambda=0.068N(0)$ in superconductivity, where $N(0)$ is the electron density of states per eV, spin and C_{60}. Using the values[9] of $N(0)$=8.5 and 10, we obtain λ=0.58 and 0.68 for K_3C_{60} and Rb_3C_{60}, respectively, which are of the correct order of magnitude to explain the superconducting transition temperatures within a BCS mechanism. The coupling strength entering in (1) is independent of $N(0)$. *Ab initio* calculations indicate that the overall electron phonon coupling λ relevant to the photoemission process (i.e., involving a final state in which a single electron has been removed) is applicable to superconductivity, as the A_g phonons, which are most sensitive to the charge on the C_{60} molecule, couple relatively weakly. The plasmon coupling $g_{\rm pl}$ was obtained from a tight-binding model[10] of the doped C_{60} solid by calculating the strength of the pole in the inverse dielectric function. The corresponding plasmon was broadened with a Gaussian of full width at half maximum of 0.5 eV to reproduce the experimental width.[11,12] To obtain the experimental plasmon frequency, the width of the conduction band was reduced with respect to the calculated

value and the background dielectric function was set to its experimental value[12] ($\varepsilon_\infty = 4.2$). This results in the coupling $(g_{pl}/\omega_{pl})^2 = 1.0$ for the plasmon. The Hamiltonian (1) can be solved exactly, and the resulting spectrum corresponds to photoemission from a discrete electronic level (ε). This spectrum is convoluted with a DOS representing the occupied part of the conduction band of A_3C_{60}. For simplicity, a band of the shape shown as an inset to Fig. 1 was used. The half-width of this band is reduced in comparison with the value obtained from band-structure calculations (~ 0.3 eV),[9] in order to take a polaronic type of narrowing into account. The actual bandwidth used (half-width = 0.18 eV) represents an optimal value for agreement of the calculated spectra with experiment, particularly in the region of the two low-energy peaks [i.e., up to ~ 0.4 eV binding energy (BE)]. All the calculations presented here include a broadening of 25 meV, representing the experimental energy resolution of the photoemission experiments.

The photoemission profiles of the series of Rb_xC_{60} thin films ($0 < x < 6$, to be published elsewhere) were very similar to those of K_xC_{60}.[6] The close similarity between the photoemission spectra of Rb_xC_{60} and K_xC_{60} has been pointed out previously.[13] Figure 1 shows a comparison of the low-temperature (10 K) photoemission spectra of Rb_3C_{60} and K_3C_{60} with a series of simulated photoemission spectra of A_3C_{60} (A=Rb or K). In the simulated spectra, the plasmon coupling, $(g_{pl}/\omega_{pl})^2$, is equal to the calculated result, while the coupling to the phonons is multiplied by the empirical constants 1.0 (i.e., equal to the calculated value), 1.4, and 1.8. The corresponding values of $\lambda/N(0)$ are 0.068, 0.095, and 0.122. The experimental Rb_3C_{60} spectrum has a clear peak centered at ~ 0.06 eV below E_F and is followed by a dip centred at 0.15 eV BE, with a further peak at 0.25 eV and another dip at 0.45 eV BE. There are also signs of an additional broad peak at ~ 0.6 eV BE. The spectrum of K_3C_{60} is very similar. For both materials, the spectra for $T = 10$ K have a sharp onset due to emission from the HOMO-derived band of C_{60} at ~ 1.5 eV BE and the width of the occupied conduction-band-derived spectral weight is ~ 1.3 eV. It is clearly seen from the figure that the best agreement between the calculation and the experimental spectra is achieved with a value of $\lambda = 0.095N(0)$, which gives values of $\lambda = 0.82$ and 0.95, taking[9] $N(0) = 8.5$ and 10 for K_3C_{60} and Rb_3C_3, respectively. Thus λ is a factor of 1.4 larger than the value arrived at from the *ab initio* calculation. We note, however, that the low BE part of the calculated spectrum (up to ~ 0.4 eV) is sensitive to the assumed shape of the conduction-band DOS, and thus care is needed in the determination of λ from the photoemission data. In the course of the measurements shown in Fig. 1, spectra of K_3C_{60} were recorded at 10 K as a function of the polar angle of off-take of the photoelectrons from the surface normal (Θ). No major changes were found in the intensity at the Fermi edge or in the general shape of the conduction-band emission as Θ was varied between 0° (normal emission) to 75°.

The temperature dependence of the conduction-band spectral weight of a sample of Rb_xC_{60} with x close to three is shown in Fig. 2. The room-temperature spectrum is very similar to that observed previously for K_3C_{60}.[6] There is an indication of a narrow peak just below E_F, but in comparison to the $T = 10$ K spectrum, the structures at higher energies are significantly washed out. Interestingly, the onset of emission from the HOMO-derived spectral weight is also considerably broadened at $T = 300$ K, in comparison with the $T = 10$ K spectrum. The upper trace in Fig. 2 shows the spectrum of the same sample heated to 425 K. At this temperature, there is no sign of the peak near the Fermi level. Instead, the DOS at E_F is considerably reduced and the spectrum is dominated by a broad, featureless peak centered at ~ 0.5 eV BE. The breadth of the emission onset of the HOMO-derived spectral weight is also much increased. Significantly, the temperature-dependent changes of the photoemission profile of the conduction

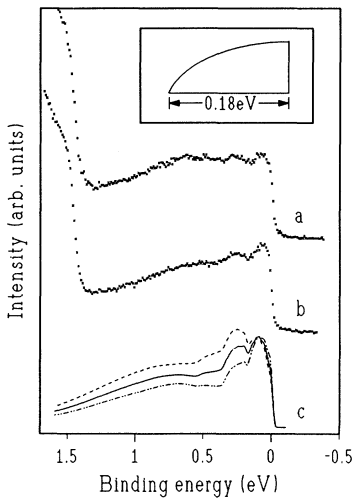

FIG. 1. Photoemission spectra of (a) K_3C_{60} and (b) Rb_3C_{60} recorded at 10 K. Also shown in (c) are calculated photoemission spectra of A_3C_{60} (A=Rb or K) with electron phonon coupling constants, $\lambda/N(0)$, of 0.068 (dotted-dashed line), 0.095 (solid line), and 0.112 (dashed line). The inset shows the form of the half-filled conduction band used in the calculation.

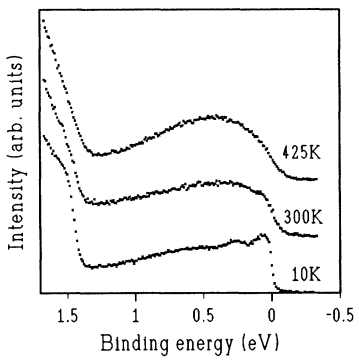

FIG. 2. Photoemission spectra of Rb_3C_{60} as a function of temperature.

band of Rb_3C_{60} illustrated in Fig. 2 are completely reversible on cycling of the temperature between 10, 300, and 425 K. Analogous results were also recorded for K_3C_{60} (not shown). No changes in the spectra of undoped[6] and fully doped A_6C_{60} were observed between 10 K and room temperature.

Analysis of the occupied conduction-band spectra shown in Fig. 1, assuming the total spectral weight represents three electronic states, leads to a DOS at E_F of 3.1 and 4.1 states/eV C_{60} for K_3C_{60} and Rb_3C_{60}, respectively. These figures are lower than those from band-structure calculations[9] or NMR (Refs. 14 and 15) and suggest that the spectra of Fig. 1 may not be a true reflection of the conduction-band density of states, but rather the spectral function including phonon and plasmon satellites. It has been suggested that the discrepancy between the DOS at E_F determined from photoemission and from bulk sensitive techniques is a result of the short inelastic mean free path in photoemission when compared to the diameter of the C_{60} molecular unit and the presence of a nonmetallic surface layer.[16] In a simple picture, the effective escape depth of the emitted photoelectrons for off-normal emission is reduced by a factor $\cos\Theta$, with respect to the appropriate value at normal emission. Thus, the data for K_3C_{60} mentioned earlier recorded with $\Theta=75°$ are correspondingly more surface sensitive (by a factor of ~ 4) than those at normal emission. The lack of dependence of the conduction-band structure or DOS at E_F on the angle of photoelectron off-take, together with the observed scaling of the intensity of the K $3p$ shallow core level with the corrected K $2p$/C $1s$ core-level ratio from Mg $K\alpha$ XPS in a previous study,[6] suggests that the composition and electronic structure of K_xC_{60} at the surface is representative of that in the bulk.

Recently, structure similar to that observed in Fig. 1 has been reported in low-temperature photoemission[7] of K-doped C_{60}(111). In this study, it was suggested that the fine structure could be attributed to a combination of phonon satellites together with transfer of spectral weight from the quasiparticle peak at E_F due to the effects of electron correlation. The calculated spectra in Fig. 1 clearly show that the photoemission spectra are consistent with the coupling of the electronic system, during the photoemission process, to both the on-ball molecular vibrations of C_{60} and the charge-carrier plasmon. Moreover, the strength of the electron-phonon coupling required for an accurate description of this structure is sufficient to explain the superconducting transition temperatures of the two fullerides within a conventional phonon-mediated mechanism. In this manner we are able to explain both the previously anomalous bandwidth and DOS at E_F observed for A_3C_{60}. These results do not exclude, however, that other many-body effects may also be of importance.

The temperature dependence of the conduction-band photoemission profile of Rb_3C_{60} shown in Fig. 2 is more difficult to understand. A simple fitting procedure, including termination of the lowest-energy peak of the $T=10$ K spectrum with a Fermi edge, shows that the decrease in the DOS at E_F and progressive smearing out structure at higher energy as the temperature is increased is not solely the result of changes in the Fermi-Dirac distribution. Changing the temperature will only alter the population of phonons in the electronic ground state with energies comparable to k_BT. Calculations including the A_g and H_g molecular phonons (with a harmonic approximation with linear coupling), indicate that this process cannot account for the strong observed temperature dependence of the photoemission spectral weight, as these phonons are too high in energy. Whether the excitation of large numbers of low-energy intermolecular anharmonic phonons, alkali-metal optical phonons, or librations could explain the temperature dependence is open to discussion.

From analogy with bulk studies,[17] no phase changes would be expected to occur across the temperature range studied here if the Rb_3C_{60} film was stoichiometric. If the sample was Rb deficient than phase separation between phases with $x=1$ and 3 may occur, with the Rb_1C_{60} phase favored at elevated temperatures.[18] Similarly, separation between $x=3$, 4, and 6 phases may be proposed for samples with $x>3$. In addition, the possibility of nonequilibrium growth of A_xC_{60} films has been proposed.[7] If other phases were present in our sample and their conduction-band DOS differed markedly from that of Rb_3C_{60}, then it is possible that the behavior seen in Fig. 2 results from reversible temperature-dependent changes in the relative amounts of each composition present. However, the data of Fig. 2 show a progressive change in conduction-band spectral weight as the temperature is altered, rather than the discontinuous behavior that would result from a single temperature-dependent phase transition. Furthermore, although the phase diagram of K_3C_{60} may reasonably be expected to differ from that of Rb_3C_{60}, K_3C_{60} shows essentially the same temperature dependence as the Rb fulleride, suggesting a common origin for the temperature dependence in the two materials.

It is interesting to note that, in contrast to the situation in the undoped material,[6] the onset of the spectral weight derived from the HOMO levels of C_{60} (~ 1.5 eV BE in Fig. 2) also shows a temperature dependence. This onset sharpens as the temperature is decreased, and at 10 K is more abrupt than the corresponding edge of the HOMO of C_{60} at the same temperature.[6] This may result from the existence of a distribution of slightly different Fermi-level positions in the grains of the undoped C_{60} film leading to a smearing out of the HOMO edge.

In conclusion, the anomalous width of the spectral weight, the low DOS at E_F, and the fine structure observed in low-temperature photoemission from A_3C_{60} (A=K and Rb) has been shown to be consistent with the presence of satellites due to coupling to both phonons and the charge-carrier plasmon.

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