

## Electron energy-loss and photoemission studies of solid C<sub>84</sub>

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The electronic structure of pure solid C<sub>84</sub> has been studied using high-energy electron energy-loss spectroscopy in transmission and photoemission spectroscopy. Information is obtained on the occupied and unoccupied  $\sigma$  and  $\pi$  bands. The reduced degeneracy of the electronic states and smaller band gap of C<sub>84</sub> in comparison with C<sub>60</sub> are evident, as well as the excitonic nature of the transition across the band gap of solid C<sub>84</sub>.

### I. INTRODUCTION

Several years after the first preparation of bulk quantities of C<sub>60</sub>,<sup>1</sup> it still remains a formidable practical challenge to separate and purify macroscopic amounts of the higher fullerenes C<sub>x</sub>, particularly for  $x > 70$ . Consequently, in contrast to the case of C<sub>60</sub> and C<sub>70</sub>, there have been relatively few studies of the structure and properties of the third most abundant fullerene, C<sub>84</sub>, in the solid state. However, advances in separation techniques have meant that purified higher fullerenes have become available and have been studied using a number of techniques including <sup>13</sup>C NMR,<sup>2</sup> ultraviolet/visible absorption,<sup>3</sup> and ultraviolet<sup>4</sup> (uv) and x-ray photoelectron spectroscopy (XPS).<sup>5</sup> Ordered thin films of C<sub>84</sub> can be grown on mica, which are face centered cubic (fcc) with a lattice constant  $a_0 = 15.9 \text{ \AA}$ .<sup>6</sup> Recently, results from an electron energy-loss spectroscopy (EELS) in transmission study of C<sub>84</sub> were reported.<sup>7</sup>

There are a large number of possible fullerene structural isomers of C<sub>84</sub>, but it appears from NMR studies that the samples from different laboratories are remarkably similar.<sup>2</sup> The consensus is that there are  $D_{2d}(23)$  and  $D_2(5 \text{ or } 22)$  isomers<sup>8</sup> in the ratio 1:2, with the  $D_2(22)$  isomer thought to be the energetically favored  $D_2$  form.<sup>9</sup>

In this paper, we report an investigation of the solid state electronic structure of well characterized C<sub>84</sub> thin films using EELS in transmission and high-resolution photoemission spectroscopy (PES). Our results show that the general features of the electronic structure of C<sub>84</sub> are similar or analogous to those of C<sub>60</sub>. However, in comparison with C<sub>60</sub>, the lower molecular symmetry and correspondingly lower degeneracy of the electronic levels do result in significant reductions in both the sharpness of the electronic bands in C<sub>84</sub>, and the magnitude of the fundamental gap.

### II. EXPERIMENT

C<sub>84</sub> of purity 97.5% by weight was prepared using state-of-the-art liquid chromatographic treatment of fullerene-containing carbon soot produced using the Krätschmer/Huffman gas discharge method.<sup>1</sup> Details of the separation, purification, and characterization procedures will be published elsewhere.<sup>10</sup>

The thin films for EELS investigations ( $\sim 1000 \text{ \AA}$  thick) were prepared by sublimation of C<sub>84</sub> at  $\sim 550 \text{ }^\circ\text{C}$  from a copper crucible onto KBr single crystal substrates held at  $140 \text{ }^\circ\text{C}$  in a vacuum chamber with base pressure  $5 \times 10^{-9}$  mbar. The films were subsequently floated off the substrates in distilled water, mounted on standard electron microscopy grids, and immediately transferred to the EELS spectrometer (base pressure  $3 \times 10^{-9}$  mbar) in which they were annealed *in vacuo* at  $350 \text{ }^\circ\text{C}$ . The same free-standing films were also characterized using transmission electron microscopy (TEM). The energy-loss as well as electron diffraction data were recorded at room temperature in transmission using a spectrometer<sup>11</sup> having a primary beam energy of 170 keV. The energy resolution of the spectrometer was set to 0.14 eV. The momentum resolution was chosen to be  $0.04 \text{ \AA}^{-1}$  for the valence band excitations and elastic scattering (electron diffraction) measurements, and  $0.20 \text{ \AA}^{-1}$  for the C 1s core excitations.

For the photoemission measurements, C<sub>84</sub> was sublimed from a well-degassed Knudsen cell at  $500 \text{ }^\circ\text{C}$  onto a freshly evaporated gold film held at room temperature. The film thickness was  $\sim 40 \text{ \AA}$ , deposited at a rate of  $\sim 0.6 \text{ \AA}/\text{min}$ , as determined by a quartz crystal thickness monitor. After deposition, the C<sub>84</sub> was annealed at  $150 \text{ }^\circ\text{C}$  for 1 h to improve crystallinity. The photoemission spectra were recorded using He I radiation ( $h\nu = 21.22 \text{ eV}$ ), with a total energy resolution of 25 meV. Both the resolution

and the position of the Fermi level of the spectrometer (and hence the sample) were monitored using measurements on a clean Au film at 15 K. The data shown here contain no correction for He I satellite lines.

### III. RESULTS

From analysis of the TEM data (not shown), as well as electron diffraction experiments carried out *in situ* in the EELS spectrometer, the  $C_{84}$  thin films grown on KBr present a (111) surface of a face centered cubic (fcc) lattice with  $a_0 = 15.8 \text{ \AA}$ . Within error, this is identical to the result of Saito *et al.*<sup>6</sup> from films grown on mica. The TEM images revealed that the films were comprised of mainly single-domain ordered regions of average extension  $\sim 700 \text{ \AA}$ , which is slightly larger than the domain size reported by Saito *et al.*<sup>6</sup>

In Fig. 1 we show the loss function  $\text{Im}(-1/\epsilon)$  of  $C_{84}$  for small momentum transfer ( $q=0.1 \text{ \AA}^{-1}$ ). After subtraction of the contributions from the direct beam and multiple scattering,<sup>12</sup> the absolute value of the loss function can be obtained from a Kramers-Kronig analysis. This provides the real and imaginary part of the dielectric function,  $\epsilon_1$  and  $\epsilon_2$ , respectively. These quantities are also shown in Fig. 1. For the purposes of comparison with present and future optical data, we have also evaluated the optical conductivity  $\sigma(\omega)$ . This can be seen in the bottom panel of Fig. 1.

The low-energy excitations of  $C_{84}$  shown in Fig. 1 contain two main groups of features.<sup>7</sup> The first of these is located at energies less than  $\sim 10 \text{ eV}$  with a maximum at

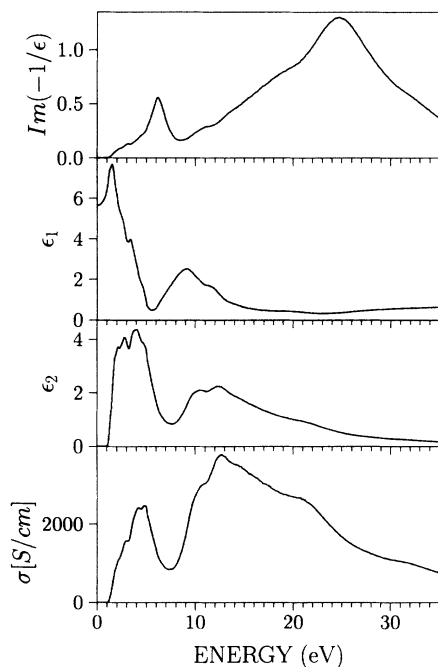


FIG. 1. The loss function  $\text{Im}(-1/\epsilon)$ , the real and imaginary parts of the dielectric constant,  $\epsilon_1$  and  $\epsilon_2$ , and the optical conductivity  $\sigma(\omega)$  of solid  $C_{84}$ . The momentum transfer is  $0.1 \text{ \AA}^{-1}$ .

$\sim 6.2 \text{ eV}$  in the loss function, while the second set of features at higher energy is centered on a peak at  $\sim 24.6 \text{ eV}$ . We note that a clear gap is observed at low energy, with an onset in the loss function at  $1.2 \pm 0.1 \text{ eV}$ , in agreement with Kuzuo *et al.*<sup>7</sup>

The C 1s core level excitations of  $C_{84}$  can be seen in Fig. 2. Neglecting the effect of the core hole, these excitations from the C 1s level into C 2p-derived bands are related to the unoccupied density of states (DOS) having C 2p character. The onset of the C 1s transitions in  $C_{84}$  is  $283.7 \text{ eV}$ . The first peak is found at  $284 \text{ eV}$ , followed by a broad peak with a maximum at  $\sim 285.9 \text{ eV}$  which has three shoulders at lower energy ( $\sim 284.7$ ,  $\sim 285.2$ , and  $\sim 285.6 \text{ eV}$ ). There then follows a weak maximum at  $\sim 287.3 \text{ eV}$  and a steplike structure at  $\sim 290 \text{ eV}$ .

The photoemission spectra of  $C_{84}$  as a function of temperature are shown in Fig. 3. In the room temperature spectrum, the onset of spectral weight is located at a binding energy (BE) of  $1.3 \text{ eV}$ , with maxima at  $2.1$ ,  $3.4$ ,  $5.4$ ,  $6.4$ , and  $7.8 \text{ eV}$  BE. Further bands are evident as shoulders on the main peaks, located at  $1.7$ ,  $3.1$ ,  $4.5$ ,  $5.1$ , and  $8.5 \text{ eV}$  BE. These results are broadly in agreement with an earlier photoemission study of  $C_{84}$ ,<sup>4</sup> although the superior energy resolution and statistics of the present data allow the discrimination of more features with greater certainty. The widths of the leading features are estimated from peak fitting to be  $1.3$  and  $1.4 \text{ eV}$ . It can be seen that there are no great changes in the spectral profile across the measured temperature range.

### IV. DISCUSSION

Before discussing the valence band excitations shown in Fig. 1 in detail, it would be useful to consider the assumptions made in applying the Kramers-Kronig analysis to the loss function. To perform the Kramers-Kronig analysis, the absolute scale of the loss function has to be known. This is usually determined either from prior knowledge of the value of  $\epsilon_1(0)$  from another source, or from the value required for agreement with the oscillator strength sum rule, in which the effective density of valence electrons,  $n_{\text{eff}}$ , is related to the imaginary part of the dielectric function,  $\epsilon_2$ , by the following relation:

$$n_{\text{eff}} = \frac{m}{2\pi^2 e^2} \int_0^\infty E \epsilon_2(E) dE, \quad (1)$$

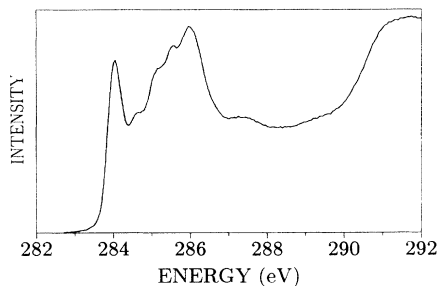


FIG. 2. C 1s absorption edge for  $C_{84}$ .

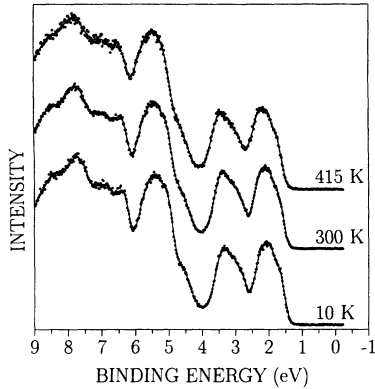


FIG. 3. He I photoemission spectra of  $C_{84}$  as a function of temperature. The solid lines are intended as a guide to the eye.

in which  $E$  is the energy and  $m$  the electron mass. For  $C_{60}$ , the value of  $\epsilon_1(0) = 4.2$  is known from ellipsometric measurements.<sup>13</sup> This allows the experimental derivation of  $n_{\text{eff}}$  for  $C_{60}$ ,<sup>14</sup> which is found to be 10% lower than that arrived at from the total number of valence electrons ( $4n_C$ , where  $n_C$  is the number of carbon atoms) and the volume of the unit cell.<sup>15</sup> To the best of our knowledge no direct experimental value of  $\epsilon_1(0)$  has been determined for  $C_{84}$ ; thus, by analogy with  $C_{60}$ , we scale the loss function using the sum rule (1), taking  $n_{\text{eff}}$ , as in  $C_{60}$ , to be 10% lower than the value derived from  $4n_C$  and the unit cell volume. This results in  $\epsilon_1(0) = 5\text{--}6$  for  $C_{84}$ , taking a fcc unit cell with  $a_0 = 15.8$  Å. This value of  $\epsilon_1(0)$  is higher than that of  $C_{60}$ , which is in keeping with the smaller band gap of the higher fullerene.

The loss function of  $C_{84}$  seen in Fig. 1 displays two main features familiar from the spectra of other  $\pi$ -bonded carbon systems such as  $C_{60}$  and  $C_{70}$ ,<sup>14</sup> graphite,<sup>11</sup> and polyacetylene.<sup>11</sup> In these compounds, the prominent peak in the region of 20 eV (24.6 eV in  $C_{84}$ ) is ascribed to a collective excitation of the total  $\pi + \sigma$  valence electron system. The preceding structure with a maximum near 6 eV is the corresponding plasmon of the  $\pi$  electrons alone (this appears at  $\sim 6.2$  eV in  $C_{84}$ ). In  $C_{84}$ , both of these features appear at slightly different energies than in  $C_{60}$ . In common with  $C_{60}$ , the energy of the  $\pi$  and  $\pi + \sigma$  plasmons observed in  $C_{84}$  cannot be correctly reproduced within calculations based on the Drude model alone.<sup>14,16</sup> Assuming the same electron density as was used in the Kramers-Kronig analysis of the loss function discussed above, the Drude model predicts the energy of the  $\pi + \sigma$  plasmon of  $C_{84}$  to be  $\sim 20$  eV, some 5 eV lower than is experimentally observed. However, the energy of the plasmon,  $E_p$ , can be more satisfactorily calculated using a Drude-Lorentz model,<sup>14</sup> which gives  $E_p = (E_g^2 + 4\pi n_{\text{eff}} e^2 \hbar^2 / m)^{1/2}$ , in which the presence of oscillators at an energy greater than zero,  $E_g$ , is included. In this model, we achieve good agreement with the experimental plasmon energy (25 eV) taking  $E_g \sim 14$  eV. This value is reasonable in light of the optical conductivity data shown in Fig. 1, in which the largest contribution to the oscillator strength, due to  $\sigma \rightarrow \sigma^*$  transitions, is

situated between  $\sim 8$  and 35 eV and has a maximum at  $\sim 14$  eV. The value of the onset in the loss function closely resembles the gap value obtained from uv absorption measurements of  $C_{84}$  in solution ( $\sim 1.2$  eV),<sup>3</sup> as well as that from C 1s core level photoemission shakeup satellite structure ( $\sim 1.4$  eV).<sup>5</sup> The similarity of the size of the solution and solid state gap points to the molecular nature of the latter transition in solid  $C_{84}$ . These gap values are smaller than those of solid  $C_{60}$ ,<sup>14,17</sup> and result from the reduction of the  $\pi$ - $\pi^*$  energy level separation as a consequence of the lower degeneracy in the higher fullerene.

The C 1s absorption spectrum shown in Fig. 2 represents transitions from the C 1s core level into the bands derived from the unoccupied  $\pi^*$  and  $\sigma^*$  molecular orbitals of the  $C_{84}$  molecules in the solid [i.e., C 1s  $\rightarrow$  LUMO (lowest unoccupied molecular orbital), LUMO+1, LUMO+2, etc.]. There is a pronounced minimum between the first feature due to C 1s  $\rightarrow$  LUMO transitions and the higher excitation channels, together with clear fine structure in the latter. These details were not observed in an earlier EELS study of  $C_{84}$ .<sup>7</sup> However, the C 1s absorption spectrum of  $C_{84}$  still shows less distinct spectral features than is the case for  $C_{60}$ .<sup>14</sup> This is a consequence of the lower symmetry of  $C_{84}$  with respect to  $C_{60}$ , and thus of the lower degeneracy of the electronic levels of the higher fullerene. In particular, the structure observed at energies above the C 1s  $\rightarrow$  LUMO peak (i.e., between 286 and 290 eV) in  $C_{60}$  is smeared out in  $C_{84}$ . Additionally, the relative intensity of the first peak (C 1s  $\rightarrow$  LUMO) is also lower in  $C_{84}$  than in  $C_{60}$ . This last point results, at least in part, from the presence of a minimum of 32 inequivalent carbon sites in the solid resulting from the  $C_{84}$  isomer mixture in the sample. From analogy with graphite<sup>11</sup> and  $C_{60}$ ,<sup>14</sup> the steplike structure at  $\sim 290$  eV is assigned to the onset of transitions from the C 1s level to the unoccupied  $\sigma^*$ -derived bands.

Turning to the photoemission spectra shown in Fig. 3, the width of the features in the  $C_{84}$  spectrum, and in particular the two peaks at lowest BE, is greater than in  $C_{60}$  [in which the highest occupied molecular orbital (HOMO) and HOMO-1 have widths 1.0 and 1.2 eV, respectively<sup>18</sup>]. At this stage it is difficult to definitively assign the observed peaks in the photoemission spectrum to bands derived from particular molecular orbitals of  $C_{84}$ . This follows from both the polyisomeric nature of the sample, and the high degree of overlap between the different features in the spectrum (which in turn results from the relatively low degeneracy of the molecular energy levels of  $C_{84}$ ). However, by analogy with  $C_{60}$ , and together with the photon-energy-dependent photoemission data of  $C_{84}$  from Hino *et al.*,<sup>4</sup> it would appear likely that at least the first two features are derived from the uppermost groups of  $\pi$ -bonding molecular orbitals.

The onset of the occupied DOS of  $C_{84}$  seen in Fig. 3 is at 1.3 eV BE. In inverse photoemission (IPES), the onset of the first unoccupied band of  $C_{84}$  is found at 0.4 eV above  $E_F$ .<sup>19</sup> Thus the gap from PES and IPES is  $\sim 1.7$  eV. This quantity is a measure of the gap between the  $(N - 1)$  and  $(N + 1)$  electronic states, where  $N$  is the number of electrons in the ground state electronic

configuration of  $C_{84}$ , and represents the energy gap that needs to be overcome in the transport of electrical current through the material. In  $C_{60}$ , this so-called transport gap is  $\sim 2.3$  eV and is some 0.8 eV higher than the gap value from optical or EELS studies of solid  $C_{60}$ .<sup>20,21</sup> Thus, as expected,  $C_{84}$  has a smaller gap between the occupied and unoccupied bands derived from the molecular orbitals than  $C_{60}$ . Additionally, in  $C_{60}$  this discrepancy between the PES-IPES gap and the EELS gap is taken as evidence that the low-energy excitations correspond to Frenkel-type molecular excitons. In the case of  $C_{84}$ , the transport gap from PES-IPES is  $\sim 0.5$  eV greater than that from EELS and thus it would seem that in this case too the low-energy excitation observed in EELS is excitonic in nature. This conclusion is further strengthened by the fact that the size of the gap of solid  $C_{84}$  is the same as that observed in solution.

By analogy with other fullerenes, it would be reasonable to expect that the quasispherical shape and weak intermolecular interactions in solid  $C_{84}$  would result in a significant degree of temperature-dependent orientational disorder. It is seen from Fig. 3 that the PES profile of  $C_{84}$  remains essentially unchanged on either heating (415 K) or cooling (10 K) from room temperature. This result does not necessarily preclude the existence of temperature-dependent orientational disorder in  $C_{84}$ , as similar behavior has been observed for  $C_{60}$ , in which the expected changes in the occupied DOS resulting from the solid state phase transitions were not observed in high-resolution PES.<sup>18</sup> This was suggested to be a result of a smearing out of the expected fine structure due to the excitation of phonons, possible Jahn-Teller distortion, or the existence of satellites resulting from the effects of strong correlation.<sup>18</sup> The same potential broadening mechanisms may also lead to the lack of any observed temperature dependence in the PES spectra of  $C_{84}$ . In

addition, the existence of at least two isomers may preclude the observation of phase transitions related to orientational ordering, due to the extra disorder inherent in the mixed isomer system. The apparent temperature independence of the PES profiles of  $C_{60}$  and  $C_{84}$  is in contrast to the case of  $C_{70}$ , in which several features show an enhancement in intensity above room temperature, with increasing broadening of these features as the temperature is decreased to 40 K.<sup>22</sup>

## V. CONCLUSIONS

The present study of the electronic structure of thin films of  $C_{84}$  using EELS and PES has revealed the general similarities of the electronic structures of  $C_{84}$  and  $C_{60}$ . However, the lower symmetry and thus degeneracy of the electronic levels of the former leads to the broadening of many of the features in the spectra in comparison to  $C_{60}$ . The lifting of the degeneracy in  $C_{84}$  is also evident in the smaller gap observed in the loss function (1.2 eV) compared to  $C_{60}$ . In common with  $C_{60}$ , the gap excitation in solid  $C_{84}$  is excitonic in character.

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