

## Doping of C<sub>60</sub> with iodine

SIR — The announcement by H. Sekine *et al.* of superconductivity in I- and Br-doped fullerenes generated much curiosity (see ref. 1) because iodine-fullerene mixing was not expected, based on comparison with graphite-intercalated compounds (for example, ref. 2), and because superconductivity would reflect hole doping rather than electron doping. Hole doping is particularly intriguing, given the ease with which metallic and superconducting electron-doped fullerenes can be prepared<sup>3</sup>.

We have used X-ray photoelectron spectroscopy to examine I mixing with C<sub>60</sub> and the subsequent energy-level spectrum. An ultrahigh vacuum I<sub>2</sub> dosing source was constructed, based on the electrochemical dissociation of AgI (ref. 4). Advantages of such a source are the precise control over dosing and minimal exposure of the chamber to the reactive gas. Calibration of the source was based on the saturation coverage of a cleaved GaAs(110) surface, which for Cl<sub>2</sub> is about half of a monolayer, or  $4.4 \times 10^{14}$  atoms cm<sup>-2</sup> (ref. 5). A 75-Å C<sub>60</sub> layer was formed on GaAs and annealed to about 150 °C to form a well-ordered layer, as shown by scanning tunnelling microscopy<sup>6</sup>.

Initial exposures of clean fullerene films to about  $10^{15}$  I<sub>2</sub> molecules cm<sup>-2</sup> at 100 °C showed only trace amounts of I, and analysis of the attenuation of the

GaAs and C<sub>60</sub> emission demonstrated that a small amount was intermixed with the film, with a composition of approximately C<sub>60</sub>I<sub>0.04</sub>. The effect of I incorporation was to shift the C 1s emission 0.2 eV to lower binding energy, but the spectral signatures of the fullerene showed no changes that would indicate compound formation. Instead, the changes were analogous (but in the opposite directions) to those observed following the addition of small amounts of K to C<sub>60</sub> layers, an effect related to the pinning of the Fermi level near the edge of the LUMO-derived conduction band and screening by these electrons of the core holes<sup>7</sup>. Hence, I doping induces Fermi level movement towards valence band states derived from HOMO. Depletion of valence states by acceptors should result in a dramatic decrease in the C 1s binding energy, but this was not observed, suggesting that complete charge transfer to I does not occur. The binding energy of the I 3d core level was 0.1 eV lower than both I<sub>2</sub> dissociated on the GaAs(110) surface and CdI<sub>2</sub> layers with the same linewidth, suggesting that I was atomic and at least partially ionic.

Higher exposures to I<sub>2</sub> did not increase the amount of I incorporation, in contrast to the behaviour for alkali doping, where mixing led to fulleride formation<sup>3,7</sup>. To increase the amount of I in the film, we decreased the substrate temperature and illuminated the surface during I<sub>2</sub> exposure to create excited state I<sub>2</sub>. The fullerene films were exposed to  $2 \times 10^{16}$  I<sub>2</sub> molecule cm<sup>-2</sup>, providing about 40 I atoms for each fullerene if the sticking coefficient were unity. Because the iodine signal never increases above the level formed by the initial exposure, C<sub>60</sub>I<sub>0.04</sub>, the formation of I-containing compounds from the vapour phase is highly unfavourable.

As an alternative method of providing I for mixing with C<sub>60</sub>, we deposited C<sub>60</sub> molecules onto an I-saturated GaAs surface. I was not released from the GaAs bonds into the fullerene overlayer because I mixing was not energetically favourable. Similarly, mixing was not promoted either by illumination (which would provide electrons and holes at the surface and could enhance surface chemistry) or by heating to any temperature below that needed to desorb the fullerenes.

A difficulty inherent with iodine doping from the AgI source is that the cell generates I<sub>2</sub> molecules rather than I atoms. The 1.33-Å atomic radius of I is sufficiently small that diffusion in the interstices could occur after dissociation of the larger molecule. To enhance I<sub>2</sub> dissociation before adsorption, a hot W

filament was placed in line-of-sight with the I<sub>2</sub> generator. In this case, exposure to about  $2 \times 10^{16}$  I<sub>2</sub> molecule cm<sup>-2</sup> produced an intermixed overlayer with a stoichiometry of C<sub>60</sub>I<sub>0.3</sub>. The C 1s emission was shifted rigidly to lower binding energy relative to the pure C<sub>60</sub> layer by the same amount as was observed for the C<sub>60</sub>I<sub>0.04</sub> layer formed without the filament. Much higher exposures failed to yield a measurable increase of I-C<sub>60</sub> mixing.

In summary, the exposure of fullerene layers to I from the vapour phase results in slight doping but not the formation of a distinct compound. It remains to be seen if stable phases exist, but our results suggest that electron transfer from the HOMO of C<sub>60</sub> is unlikely.

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## Kiwi's egg

SIR — Speculation has recently been revived (see S. J. Gould, *Bully for Brontosaurus*, Hutchinson Radius, 1991) on the issue of the kiwi, and how natural selection might account for its relatively enormous egg, which is of no obvious advantage to the chick and a considerable disadvantage to the hen. I suggest that we find the problem baffling only because, by the time we began wondering about it, the moa had become extinct.

Before man arrived in New Zealand, the kiwi had no mammalian predators. But large omnivorous ratites like the moa gobble up eggs laid on the ground, except those in the large clutches deposited by their own harems. A kiwi's egg added to such a clutch might escape their predation, and the bigger it was the more easily it would avoid detection and eviction. Later, when the moa vanished and the rat arrived, kiwi survivors would be those which most rapidly learned to scratch holes in the ground.

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## Mount Etna CO<sub>2</sub> may affect climate

SIR — Allard *et al.*<sup>1</sup> recently estimated current summit-crater emissions from Mount Etna of  $13 \pm 3$  Tg yr<sup>-1</sup> CO<sub>2</sub>, with a similar contribution to the atmosphere from diffuse flank emissions. Surprisingly, this yields a total CO<sub>2</sub> flux from Etna of about  $0.6 \times 10^{12}$  mol yr<sup>-1</sup>, or about 10% of the estimated global CO<sub>2</sub> flux from all metamorphic and mantle sources (about  $6 \times 10^{12}$  mol CO<sub>2</sub> yr<sup>-1</sup>, ref. 2). Etna is known to have been continuously active since at least the fourth century BC<sup>3</sup>. If Mount Etna's CO<sub>2</sub> emissions were continuous and sustained for much of its long history, then the use of a carbon-cycle model<sup>4</sup> using Berner's<sup>5</sup> non-linear weathering-rate formulation indicates that CO<sub>2</sub> fluxes from Mount Etna alone may have been responsible for about 60 of the 280 parts per million pre-industrial CO<sub>2</sub> concentration.

This suggestion implies that variability in Mount Etna's CO<sub>2</sub> emissions could have climatic consequences, producing