

## Viewpoint

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## VIEWPOINT

## Magnetism in polymeric fullerenes: a new route to organic magnetism?

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Most magnetic materials which are used in technological applications are metals, alloys or simple compounds, all based on inorganic chemistry. The search to find *organic* materials which show magnetism has three principal motivations. First, organic materials are extremely chemically tunable because of the flexibility of carbon chemistry; there is an obvious advantage in choosing a route already favoured by biological systems. Second, organic materials can possess interesting optical properties, thus allowing the possibility of devices which implement new functionality. Third, there is the pleasure of achieving something which was once thought impossible: making ferromagnetism in materials containing only s and p electrons. Heisenberg's theory of ferromagnetism [1], which introduced the concept of exchange, had explained the observation that all ferromagnets known at that time had d and f electrons. Conventional wisdom has it that, for example, carbon (containing only s and p electrons) does not have a spontaneous magnetic moment in any of its allotropes.

Organic ferromagnetism was first achieved using organic radicals called nitronyl nitroxides. Many organic radicals exist which have unpaired spins, but few are chemically stable enough to assemble into crystalline structures. Even when that is possible, aligning these spins ferromagnetically is usually difficult to achieve. Therefore, the discovery of long-range ferromagnetism in one of the crystal phases of *para*-nitrophenyl nitronyl nitroxide ( $C_{13}H_{16}N_3O_4$ ) was particularly exciting, even though the transition temperature was a disappointingly low 0.65 K [2] (though a similar material was soon found which more than doubled this record [3]). Weak ferromagnetism in a dithiadiazolyl radical ( $C_8N_3F_4S_2$ ) has been found below 36 K [4] (rising to 65 K under pressure [5]). The ordering temperature can be raised to well above room temperature by preparing 'hybrid materials' known as molecular ferromagnets in which organic groups are combined with transition metal ions [6, 7]. Here the organic groups are themselves not magnetic but are used to mediate the magnetism between transition metal ions.

A further strategy is to use carbon 'buckyballs' to make organic materials with novel properties. Certain  $C_{60}$ -containing compounds can exhibit superconductivity [8], and weak magnetism below 16 K was found in TDAE- $C_{60}$  (TDAE is tetrakis(dimethylamino)ethylene) [9], although the nature of the ordering provoked some controversy; this was found to be due to

the existence of two distinct phases of TDAE-C<sub>60</sub> which are associated with different relative orientations of the C<sub>60</sub> molecules [10]. Until recently, C<sub>60</sub> itself was not thought to be a source of magnetism, although superconductivity below 52 K has been induced in a C<sub>60</sub> film using hole injection in a field-effect transistor geometry [11] (or below 117 K in lattice-expanded C<sub>60</sub> films [12]). In pristine solid C<sub>60</sub>, the buckyballs are arranged in a face-centred cubic lattice and held together by van der Waals bonding. The application of pressure allows the production of a number of different crystalline, polymeric and amorphous phases of C<sub>60</sub> [13], one of which is a two-dimensional polymerized rhombohedral phase containing layers of covalently bonded C<sub>60</sub> molecules [14]. This phase recently showed a signature of spontaneous magnetization up to about 500 K [15], raising the possibility that an allotrope of carbon might have a room temperature spontaneous magnetization after all.

In this issue of *Journal of Physics: Condensed Matter*, Wood *et al* [16] describe a structural and magnetic study of this intriguing two-dimensional polymerized rhombohedral phase of C<sub>60</sub>, although prepared under slightly different conditions. Reports of weak magnetization in organic materials have often proved to be wrong, so the new confirmation of the earlier work [15] is extremely encouraging. More importantly, using electron microscopy and x-ray diffraction Wood *et al* show that the buckyballs are undamaged in the most magnetic phase. With higher preparation temperatures (or higher preparation pressures) the cages can collapse and an sp<sup>2</sup> amorphous phase is produced [14]; this amorphous phase could contain unpaired defects which would explain the magnetic properties. However, by demonstrating that the C<sub>60</sub> molecules are not collapsed in the most magnetic phase, Wood *et al* have ruled out this explanation of the magnetic properties and their work consequently strongly supports a model ascribing the magnetism to radical centres formed by the dangling bonds which are left following the breaking of the intermolecular bridging bonds. The mechanism for the magnetic coupling between these radical centres is not yet elucidated and the magnetization is very small and far from being uniformly distributed throughout the sample. Nevertheless, this paper demonstrates that performing careful structural studies of samples prepared at different temperatures and pressures is the right way forward to understand this effect. The lesson from TDAE-C<sub>60</sub> is that the precise orientations of the buckyballs can be of crucial importance in determining the magnetic ground state, demonstrating that combined structural and magnetic studies are definitely needed. The letter of Wood *et al* reminds us that organic materials continue to be full of surprises.

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